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# A Study of Flame Retardants for Textiles

Auerbach Associates, Inc.

Prepared For
Environmental Protection Agency

February 1976

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# A STUDY OF FLAME RETARDANTS FOR TEXTILES

## FINAL REPORT

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF TOXIC SUBSTANCES
WASHINGTON, D.C. 20460

**FEBRUARY 1976**

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16. ABSTRACT

As part of a program for identifying potential environmental hazards associated with various branchs of technology, a review of the literature on flame retardants for textiles has been prepared. Covering the periods 1954-74, more than 500 primary documents and consultations with experts have been digested and cited. Chemicals and chemical treatments which are being used or have been proposed for producing flame retardant textiles are listed and discussed. Particular attention is given to toxicological data, to observations of health effects and to studies of environmental fates and effects of the materials which are used. The report is divided into major sections in which classes of natural and man-made textiles are considered separately. Several chemicals are identified as having their major application as flame retardants for textiles. These include certain halogenated monomers, halogenated phosphate esters, and formaldehyde derivatives of phosphorus and nitrogen compounds. The need for further studies of the fate and effects of these compounds is indicated.

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# A STUDY OF FLAME RETARDANTS FOR TEXTILES

Final Report

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Project Officer
Irving J. Gruntfest

Office of Toxic Substances
Environmental Protection Agency
Washington, D.C. 20460

Prepared by

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February 1976

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Helpful consultation in Task II was provided on toxicological implications of flame retardant compounds, potential degradation products and interactions with commonly occurring chemical and biological agents by Dr. Frederic Reiders of National Medical Services, Inc.

Technical supervision was provided for the EPA Office of Toxic Substances by Dr. Farley Fisher in Task I and Dr. Irving Gruntfest in Task II.

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# SECTION I. INTRODUCTION

The advancement of U.S. technology, often accompanied by undesireable and sometimes hazardous by-products, has led to concern on the part of the federal government and the public in general over both real and potential environmental hazards. This study[1] focusses upon one segment of this issue: the potential toxic, carcinogenic, and environmental risks posed by the increasing requirements, under federal legislation, to flame retard textiles for use in apparel, upholstery, drapes, and other consumer and industrial products. The purpose of the study was to perform a comprehensive analysis. Through published literature, unpublished reports of manufacturers, review by expert consultants, and contacts with manufacturer representatives of the state-of-the-art, the study assessed predictable future trends in textile flame retardant technology, particularly as these may have an impact upon the environment or human health.

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[1] Support for this study was provided by the Contracts Management Division of the Environmental Protection Agency under contract number 68-01-2209.

The study was comprised of two phases, or tasks. Task I provided a broad picture of the kinds of flame retardants available, the extent of their use and the relative threat posed by the alternative technologies to the environment, the workers, and the community. Task II was an intensive study of the major flame retardants for man-made fibers. It was meant to develop a full profile of those particular treatments: the chemistry, production, uses, engineering problems, contamination and toxicity.

This volume, A Study of Flame Retardants for Textiles, Final Report combines the findings of both Tasks. These observations and conclusions are based on the open literature published in technical journals, text books, handbooks, review articles, unpublished research results and manufacturer trade literature, and expert opinion canvassed from industry, academia, research laboratories, and federal resources. The literature of chemistry, biology, chemical economics, environmental studies, public and industrial hygiene, and medicine is represented throughout.

Man-made textiles have emerged from this study as the most important textiles in the domestic market. For this reason, the flame retardant technology of man-made textiles is the class that was selected for the intensive investigation in Task II of this study. Halogenated polymers, trialkylated phosphates, and aromatic compounds used in manufacturing man-made fibers impart flame retardant properties to them. In a general sense, organic chemicals in these classes are known to be of environmental concern and thus further supported interest in investigating them in detail.

## 1.1 METHODOLOGY

Task I was purposely designed as a heuristic study. The earliest subtask was intended to discover the full range of textile flame retardant chemical treatments that have been proposed experimentally as well as those that have achieved commercial success. Appendix A is a classified list of all such processes identified. It is an aggregate list in that most of the treatments represented have never achieved a degree of commercial use either alone or in combination with other materials. However, future developments, particularly in the area of chemical modification of man-made fibers, could well result in the commercial application of several treatments that in today's market are merely chemical curiosities. The reality of rapid technological advancement is emphasized by two factors: over 20 million dollars a year was spent by government and industry in 1973 and 1974 alone on research to develop new flame retardants; and, the current technology, while theoretically sound, is inadequate to cope with the combined practical problems of feedstock shortages, a highly competitive market place, economical compliance with federal standards in full production operations, and a relatively limited consumer demand for flame retardant products should the treatments adversely affect the cost, or appearance, feel, drape and ease of care that we have come to expect of textile products. Not surprisingly, most experts are of the opinion that manufacturers will continue to use those flame retardant textiles that most consistently and economically meet the required flammability standards for the various products, while continuing to look for new, less expensive and more effective techniques to replace the present methods.

While recognizing the potential for drastic changes from the recent practices in flame retardant technology, our methodology was designed to follow the literature and current practice. It is assumed that the basis for improved treatments will be found in the current, well developed technologies. Economic forces outside of the technology of flame retardancy, such as shortages of petrochemical feedstocks, fluctuation of cotton prices, patterns of worldwide demand for textiles, and modifications in the Federal government product testing methodology have been noted as they were discovered in the course of the study. They have not been considered to diminish the importance of the principal treatments that have been widely used to date. Pragmatically, the importance of economic trends was greater in considering an appropriate direction for the Task II intensive study than in describing the available technologies that under varying conditions might all find some measure of practical application.

Task II zeroed in on the halogenated polymeric flame retardants, fibers containing organic phosphorus compounds, aramids and related polymers (specifically Nomex® ), and other high temperature synthetic organic fibers. The technical discussion related to Task II is Section V of this report. Sections III and IV were the result of Task I.

### 1.1.1 Search Scope

The scope of the study was quite inclusive. Descriptions of chemical treatments of textile materials with either historical, actual or potential use as flame retardants were retrieved. This included coatings and aftertreatments of fibers and fabrics as well as chemical modifications of cellulose polymers and thermoplastic polymers that as extruded fibers might be used in textile materials.

Subsequently, the study was concentrated on the treatments and materials that are now most relevant to the textile industry. Treatments of cellulose have traditionally received the most attention. Until very recently, cotton and rayon have been the major substrates. Man-made fibers, particularly non-cellulosic thermoplastic polymers have come to greater importance in the past five years and the technology for imparting flame retardancy to the man-made fibers is far more complex and diversified than for cotton and rayon. For the more defined treatments used for cellulosics, the compounds used in the principal formulations were considered directly within scope. Thus proprietary treatments including Pyrovatex (Ciba-Geigy), and finishes based on tetrakis(hydroxymethyl)phosphonium chloride were specifically researched under their component compounds and in relationship to their actual use in the textile industry. Man-made fiber modifications and treatments are not so clear. Here it was necessary for the search to be somewhat more generic. It was necessary to concentrate on the monomers most frequently mentioned as having flame retardant characteristics. In fact, it appears that many man-made polymers in combination with ammonium phosphates, antimony oxide, mordants and various monomers acting as plasticizers, stabilizers and melt inhibitors are claimed to be fire retardants by the various definitions of local and state fire codes. Many such combinations are the basis of proprietary formulations that can be used to produce textile materials that have flame retardant properties but may or may not be covered by federal controls. Greater consideration was given to identifying the "important" monomers from the point of view of their widespread use in textiles or their potential for environmental contamination. As a result, the widespread use of vinyl chloride and vinylidene chloride as the principal flame retardant monomers in modacrylic fibers, and the limited use of brominated bis-phenol A and polychlorinated biphenyl compounds are noted as "important" monomers.

Vinyl Bromide is advertised in the trade journals for its flame retardant properties but its importance in textile uses is not clear from available documentation.

Brominated phthalic esters, and polychlorinated biphenyls are potentially effective flame retardants which would be of environmental concern if they were widely used. But here again data to indicate the extent of use are not available.

For both the cellulosic and non-cellulosic treatments that have achieved an identifiable role as effective flame retardants for textiles, the study was extended into the literature of the chemical and textile industry, textile waste disposal, environmental studies, pharmacology and toxicology. In Task II the effort was extended further into the literature of these fields to look at potential problems that have not surfaced nor have been speculatively related to flame retardants by anyone to date.

### 1.1.2 Time Frame

The study stresses relevance to the current and foreseeable technology. Although the history of flame retardant textiles is easily traced in the literature back over 300 years to treatments for canvas in Paris and London theaters, books and review articles were sufficient to characterize the early developments as they relate to today's technology. Some inorganic acids and salts that have been used from the earliest times are used still. Borax-boric acid mixtures are probably the best examples. However, no attempt has been made to retrieve the primary articles for such applications. The indexes and abstracting services were searched over a ten year span and selectively for 20 years. Books and review articles published in the past 10 years were reviewed. Significant primary publications of the past 20 years were retrieved.

In the late 1960s, the U.S. Congress amended the Flammable Fabrics Act and the Federal agencies began to tighten control of the textile industry. This began the contemporary period of flame retardancy. Our study emphasizes the literature and technical achievements in the field in this contemporary period. So, while the time frame researched for this report is the period 1953 to February 1975, the inferences, stress, and interpretations are made with deference to the contemporary period beginning in 1967.

### 1.1.3 Study Resources

The resources used to conduct the literature survey includes:

- Abstracts on Health Effects of Environmental Pollutants
- Air Pollution Abstracts (APTIC)
- Annual Bibliographies of the Information Council on Fabric Flammability
- Applied Science and Technology Index
- Biological Abstracts
- Bioresearch Index
- Chemical Abstracts (Chemical Condensates)
- Chemical Economics Handbook
- Engineering Index
- Excerpta Medica
- FDA Clinical Experience Abstracts
- Index Medicus
- Science Citation Index
- Textile Technology Digest

Journals

- Current issues of over 100 journals covering:
  - Environmental science
  - Pharmacology
  - Chemistry
  - Toxicology
  - Industrial Hygiene
  - Medicine
  - Textile Technology

Primary Articles

- Over 500 primary articles, unpublished and proprietary documents, and patents were examined and indexed when relevant. Each article was cited, abstracted and duplicated. One copy of each significant article is submitted under separate cover to the EPA Project Officer.
- Citations in this report refer to the unique accession number assigned to the retrieved articles, books, monographs, supplementary documents, and government reports.

## 1.2 FLAME RETARDANTS FOR TEXTILES: AN OVERVIEW

Historically, the technology of imparting flame retardant properties to textiles has progressed in five stages. The first attempts consisted of solutions of water soluble salts applied to curtains and drapes in public buildings. The effectiveness of the various treatments was mixed. The more successful formulations are still in use for applications in which there is little chance that the product will be subjected to rain, perspiration or washing. The class of nondurable fire retardants is representative of this first stage. The second stage of development involved rendering soluble deposits insoluble within the fabric. This was an extension of the work with soluble salts. Studies involving both water soluble retardants and insoluble deposits have been carried on concurrently since about 1850. The third stage of development evolved in the 1930s and was spurred on by the outbreak of World War II. Flameproof canvas tentage for outdoor use by the military was produced with a treatment of chlorinated paraffin and an insoluble metal oxide, mostly antimony oxide as a glow inhibitor, together with a binder resin. The treatment required application from an organic solvent. About the same time the fourth stage in the development of fire retardants was beginning under the sponsorship of the U.S. Army Quartermaster and the National Research Council, National Academy of Science. The fourth stage investigators conducted basic scientific studies of the mechanism of flame retardancy. Resulting treatments were based on the chemical reaction of the fire retardant with cellulosic molecules. The hydroxyl groups of the cellulose molecule can react directly or with an acid catalyst with many fire retardants. If the fire retardant has no cellulose reactant groups it can polymerize to form an insoluble coating on the cellulose. Fire retardants can also contain both cellulose reactive groups and monomers capable of polymerization thus facilitating the simultaneous cellulosic reaction and polymerization. The modern, durable treatments of cellulosic materials discussed in Section III of this volume are products of this fourth stage of development.[2]

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[2] Drake, George L., Jr. Fire resistant textiles
In Kirk Othmer Encyclopedia of Chemical Technology
New York, John Wiley, 1966, 9, 300-315 (OTS-AA-0029).

The fifth stage of development is the contemporary era. Non-cellulosic thermoplastic polymers are becoming increasingly more important as the basic fibers used for flame retardant applications. A dramatic example of the superior position of the non-cellulosics is provided by the diminished position of cotton fiber for use in children's sleepwear since the inception of new standards, DOC/FF 3-71. In 1971 cotton supplied 78 percent, or 27 million pounds, of the fiber used to produce size 0 to 6X sleepwear. In 1973 cotton provided less than 10 percent or only 3½ million pounds. It is assumed that the expected standard for sizes 7 to 14 will have an equal effect[3]. Although research is continuing in order to improve the role of cotton[4], the emphasis seems to be on developing additives, coreactants and finishes incorporating functional groups containing one or more of these elements for thermoplastic man-made fibers and fabrics:

- Phosphorus
- Nitrogen
- Antimony
- Chlorine
- Bromine
- Boron

Generically, the common polymeric backbones are:

- Polyolefins
- Polyvinyl chloride homopolymers
- Polyester
- Acrylics and modacrylics
- Polyamides
- Phenolics
- Aromatic polyamides/aramids

The modification of these polymers by the coreaction of organic monomers bearing the effective functional groups retards the degradation of the polymers into their volatile monomers and normally gives a reduction in flammability.

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[3] Anonymous. Man-made fiber output hits new high. Chemical and Engineering News, 52 (9): 11, (1974) (OTS-AA-0341).

[4] Daigle, D.J.; et al. Modifying THP (tris (hydroxymethyl) phosphine)-amid flame retardant. American Dyestuff Reporter, 62 (6): 57-9, 80 (1973) (OTS-AA-0020).

Consequently, in a very general sense, any such monomer can be said to be a flame retardant[5].

The most recent developments have produced an entirely new class of polymers. Notably, the new structures include an aramid and a novoloid -- very high temperature aromatic polymers. Nomex and Kynol respectively are now commercially available as textiles. Other names associated with this class are polybenzimidazole (PBI), polyimides, polyimidazoles. The aramids and the novoloids have the advantage that when they eventually decompose they form an ash or char and fall away rather than melt. They avoid the afterburn affects associated with the other thermoplastic fibers that melt rather than char even though they will self extinguish if the source of ignition is removed.

### 1.2.1 Terminology

There is no clearly defined meaning for many of the terms used to describe flammability and flame retardance. As a result, some confusion is created by the interchangeable use of terms such as fire retardant, flame retardant, flame resistant, and fireproof. The meaning of these and other terms is often clear only in context. For this report the following meanings apply:

Flame retardant textile: a generic term including any fabric that will not support combustion after the source of ignition is removed. It is used synonymously for fire retardant, flame resistant, and fire resistant textiles. The textile is expected to char or melt. It includes all treatments short of fireproofing.

Fireproof textile: This term applies only to those fabrics which undergo virtually no change when exposed to flame. It is not used lightly and it is not synonymous with flame retardant.

Afterglow: A condition of flameless combustion existing after the source of ignition is removed. Not all flame retardants are afterglow inhibitors nor are afterglow inhibitors particularly efficient flame retardants. Afterglow inhibitors and flame retardants are often used in combination. Antimony oxide is the most widely used afterglow inhibitor and yet it is an inefficient flame retardant.

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[5] Creitz, Elmer C. Chemical extinction of diffusion flames as related to flameproofing of plastics. In Society of Plastics Engineers, Annual Technical Conference, Technical Papers 28th, 1970, 368 (OTS-AA-0296).

Nondurable treatment: A chemical mixture, usually applied in a water solution which imparts flame retardance to a fabric or product. These treatments are readily removed by water or perspiration and require replacement after each exposure of the textile to water.

Semidurable treatment: Chemical application of a flame retardant compound or combination of several compounds to a textile that will resist water but will not withstand dry cleaning or more than 10 launderings.

Durable treatments: Any chemical process used to impart flame retardant properties to textiles and textile products that will last without leaching through laundering and dry cleaning virtually for the life of the fabric.

These definitions are merely functional ones. Flame retardance and treatment durability are concepts involving the chemical systems, the product uses, and the testing procedures. A treatment may be considered flame retardant when tested by one method, but not another. Product design, particularly in the case of carpets and matresses, affects the pass or fail conditions as much if not more so than the chemical treatments[6,7]. The definition of durability actually must be related to the conditions of use for the textile and product. Thus, an ammonium phosphate is a completely durable treatment on cotton or rayon batting used for insulation purposes and never exposed to water or washing leaching. These definitions are intended to differentiate the levels of durability of the initial level of flame retardancy. The property of

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[6] Mandel, John; M.N. Steel; L.J. Sharman. NBS analysis of the ASTM Interlaboratory Study of DOC/FF 3-71 flammability of children's sleepwear. ASTM Standardization News, 1 (5): 8-12 (1973) (OTS-AA-0400).

[7] Roe, Richard C. The impact of the new federal flammability standards on the bedding industry. ASTM Standardization News, 1 (5): 23-25, (1973) (OTS-AA-0402).

durability to leaching generally determines the practicality of the various treatments for use in different end products.

### 1.2.2 Flame Retardance and Product End Use

As a scientific concept, flame retardance is any treatment that renders a material less flammable than a similar sample of nontreated material. In practice, this question requires that we distinguish textile products going into:

- industrial applications (automotive, airplanes, etc.)
- institutional applications (hospitals, military, hotels, nursing homes, etc.)
- consumer products (apparel, home furnishings, etc.)

Up until 1970 the military, industrial applications and public institutions provided nearly all the market for flame retardant materials. In that time the textile industry had supplied flame retardant tentage for the military and flame retardant cotton, Nomex, and the modacrylics for a great variety of institutional home furnishings and hazardous occupation protective clothing.

Since 1971 new and stringent demands upon the textile and related industries have resulted from the implementation of the Flammable Fabrics Act of 1967 which covers specific products that the general public as consumers will purchase for personal use at the retail counter[8]. To date, Federal Testing Standards regulated by the Consumer Product Safety Commission determine the flammability performance of carpets (FF/1-70, FF/2-70), children's sleepwear, sizes 0-6X (FF 3-71) and mattresses (FF/4-72). Several standards are pending covering childrens sleepwear 7-14 (FF/5-75) and blankets. Jurisdiction for testing has been transferred to the Consumer Product Safety Commission, from the Department of Commerce.

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[8] Baum, Burton M. Flame retardant fabrics. I. Problem and solution via flame-resistant fibers. Chem. Technol., 3 (3): 167-70, (1973) (OTS-AA-0005).

Children's nightgowns, pajamas and bed robes, until the implementation of the standards, had been 90% cotton. Because the flammability standards includes the requirement that the flame retardance be tested after 50 machine washes and following 30 minutes drying at very high temperatures, the flame retardant cottons have generally been found inadequate to meet consumer product requirements. Chlorine bleaching, the use of soap and the deposit of calcium salts, all reduce the flame retardant properties.[9,10]

As a result, fibers such as the modacrylics, flame retardant acetate and triacetate, flame retardant polyesters and blends of these fibers all of which have inherent properties favorable to meeting the standards have become a major factor in these end uses where they have never been used before. Even as a blended component, cotton is not a factor since blends of cotton and man-made fibers tend to be more difficult to flame retard than either fiber alone alone[11,12,13].

Even prior to the current, severe petrochemical feedstock shortages, the demand for man-made fibers had exceeded world-wide production capacity. Polyester fibers are in the greatest demand. The result is a worldwide shortage of these fibers for flame retardant textiles[14].

Currently, the fiber producers are spending more money on the development of new and improved flame retardant man-made fibers than on any other phase of technology and development. Treatments for polyester fibers are receiving particular attention as a broad variety of tetrabromophthalimides

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[9] Perkins, R.M.; G.L. Drake, Jr., W.A. Reeves. Effect of laundering variables on the flame retardancy of cotton fabrics. Colourage, 18 (24): 33-6 (1971) (OTS-AA-0222).

[10] Perkins, R.M.; G.L. Drake, Jr., W.A. Reeves. Effect of laundering variables on the flame retardancy of cotton fabrics. Journal of American Oil Chemists Society, 48 (7): 330-3 (1971) (OTS-AA-0223).

[11] Tesoro, Giuliana C.; C.H. Meiser. Effects of chemical composition on the flammability behavior of textiles. Textile Research Journal, 40 (5): 430-6 (1970) (OTS-AA-0197).

[12] Tesoro, Giuliana C.; J. Rivlin. Flammability behavior of experimental blends. Textile Chemist & Colorist, 3 (7): 156-60 (1971) (OTS-AA-0198).

[13] Tesoro, Giuliana C.; S.B. Sello, J.J. Willard. Nitrogen-phosphorus synergism in flame-retardant cellulose. Textile Res. Jour., 39(2): 180-90 (1969)(OTS-AA-0199)

[14] Anon. Worldwide boom in textile goods spins prosperity for fiber firms. Chemical Week, 113, (2): 18-19 (1973) (OTS-AA-0391).

have been reported to impart flame retardance to polyesters[15,16]. When other end uses such as upholstery, blankets, drapery and general apparel are covered by standards, there will be an even greater demand for flame retardant, man-made fibers if those standards follow the patterns set earlier.

At the same time, at least one major chemical company, American Cyanamid, as recently as late 1973 was planning a major capital investment in a phosphine based flame retardant process for cotton products. They claim it is durable, produces a soft hand and a pliant product. Volume production of phosphine is claimed to be the key to an inexpensive process[17]. In a separate investigation, a cotton treatment based on tetrakis (hydroxymethyl) phosphine (THP), methoylolurea, and trimethylolmelamine (TMM) was found to be durable through 50 launderings and passed the FF/3-71 test for children's sleepwear. However, these finishes are still susceptable to chlorine bleaching. Developments such as these could have a significant effect on the future direction of the textile industry.

The factors controlling the industry response both in product design and in the research laboratory, are those that affect fashion, aesthetics, comfort and general performance requirements expected by consumers while achieving the flame resistance demanded by government regulations.

### 1.2.3 Mechanism of Flame Retardance

This section presents a brief review of the mechanisms by which flame retardance is generally achieved. It is intended to explain the general principles or reactivity governing the relative effectiveness of compounds shown to enhance flame retardance. Theories on pyrolysis of textile materials and oxidative degradation studies have not been a significant factor in this study. However, the mechanism of action can differ depending on the type of compound used as a flame retardant. The mechanism affects the generation of products of combustion, some of which are potentially corrosive and toxic.

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[15] Spatz, Sydney M.; H. Stone. Some N-substituted tetrabromophthalimide fire-retardant additives. Industrial & Engineering Chem. Prod. Res. & Dev., 8 (4): 397-8, (1969) (OTS-AA-0193).

[16] Anon. Flammability reduced in polyester fibers. Chemical & Engineering News, 51 (22): 27, (1973) (OTS-AA-0396).

[17] Anon. Pursuing a hot market. Chemical Week, 112 (20): 24-25 (1973) (OTS-AA-0393)

[18] Refer to note 4, page 1-8.

The mechanism for imparting durable flame retardance to cellulose is that of increasing the quantity of carbon, or char, formed instead of volatile products of combustion, and flammable tars. Salts that dissociate to form acids or bases upon heating are usually effective fire retardants. Salts of strong acids and weak bases are the most effective compounds, ammonium and amine salts are generally effective. Lewis acids and bases, either by themselves or formed in combustion are also effective.[19]

One mechanism of imparting decreased flammability to the thermoplastic materials is to lower the melting point below the decomposition point of the flame retardant chemical. This results in the formation of free radical inhibitors in the flame front and causes the material to recede from the flame without burning.[20]

Free radical inhibition involves the reduction of gaseous fuels generated by burning materials. Heating of combustible materials results in the generation of hydrogen, oxygen, hydroxide and peroxide radicals that are subsequently oxidized with flame. Certain flame retardants act to trap these radicals and snuff out the flame. Halogens, and bromine is more effective than chlorine, are particularly effective. One reaction is, for example:

$$RBr + H\cdot \longrightarrow HBr + R\cdot$$

If the resulting compound R is less readily oxidized than the radical that is removed, the result is reduced flammability.[21]

The role of phosphorus compounds has been extensively studied. In both cellulose and the thermoplastics, phosphorus salts of volatile metals, and most organophosphorus compounds are known to be effective flame retardants. The formation of char appears to be the key. For example, where triphenylphosphate, triphenyl phosphite, and triphenylphosphine are all equivalent on a phosphorus basis, the more effective flame retardant compounds act by forming phosphoric acid which results in changing the course of the decomposition of cellulose to form carbon and water.[22,23]

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[19] Baitinger, William F. Cellulose reactive fire retardants. Textile Chemist and Colorist, 4 (7): 172-6, (1972) (OTS-AA-0336).

[20] Fenimore, C. P.; F. J. Martin. Flammability of polymers. Combustion and Flame, 10 (2): 13509 (1966) (OTS-AA-0037).

[21] Ibid.

The hazardous nature of many of these acidic ingredients at the formulation stage, in waste by-products and as products of combustion is well known as they have long been used. Therefore, they are usually applied in moderate concentrations and in protected equipment. However, the application of these potentially corrosive ingredients in the wet phase of finishing mill processes in a concentrated environment represents a very distinct hazard of progressive corrosion. Ventilation and scrubbing operations used to remove these acids from the materials and processing plants can add to air and water pollution in the neighborhood of the plant. The inorganic flame retardants, particularly ammonium phosphates, represent a very undesirable component of stream pollution, if indeed they are present in significant amounts in the effluent of the textile producing plants.[24] The residue of organophosphorus chars resulting from the reclamation of junk automobiles, municipal incinerators, or as a result of a major fire in a public building where flame retardant furnishings have been used extensively might also be considered as potential pollutants. Another consideration of the increased use of flame retardant materials compared to when none are used is the increased production of smoke, carbon dioxide and toxic carbon monoxide in the immediate environment where such materials are burned. Incineration of flame retardant materials for trash disposal or in a holocause may produce a greater concentration of these by-products than comparable non-flame retardant materials.[25,26]

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[22] Refer to note 2, page 1-7.

[23] Refer to note 5, page 1-9.

[24] Mark, H.; S.M. Atlas. Environmental hazards of modern textile finishing. In H. Mark. Chemical after-treatment of textiles. Interscience, N.Y., 1971, 631-4 (OTS-AA-0348).

[25] Carroll-Porczynski, C.Z. Application of simultaneous DTA/TG and DTA/MS analysis for predicting in advance of processing the flammability and toxicity of gases of composite textile fabrics and polymers. In Thermal Analysis, Proceedings of the International Conference on Thermal Analysis 3rd, 1971, (pub. 1972), 3, 273-84 (OTS-AA-0281).

[26] Carroll-Porczynski, C.Z. Fabric flammability. New texting methods and equipment. Textile Institute and Industry, 9 (7): 188-94, (1971) (OTS-AA-0300).

The environmental considerations discussed in this section pertain to all flame retardants by virtue of their chemical mechanism of action. Specific reactions relating to individual treatments are discussed in the appropriate sections to follow.

## 1.3 ORGANIZATION OF THE REPORT

The remainder of this report is organized into the following sections:

II SUMMARY AND CONCLUSIONS
III NONDURABLE TREATMENTS
IV DURABLE AND SEMIDURABLE TREATMENTS
V MAN-MADE TEXTILES

Sections III and IV deal mostly with natural fibers, and cellulosics, particularly cotton, are the most important.

Flame retardance involving man-made fibers is significantly different from natural fibers to be treated as a separate section. Section V deals with flame retardance of man-made fibers.

The emphasis in each chapter is on the important treatments for that class of flame retardants. Either technical superiority of a treatment or its apparent potential for environmental side effects defines an important treatment.

# SECTION II. SUMMARY AND CONCLUSIONS

This section is a condensation of the full report. It consists of a brief overview of the project and the findings, conclusions and recommendations regarding non-durable and durable flame retardant treatments, mostly applicable to cotton; and, it reviews the state of flame retardance technology for man-made textiles.

## 2.1 STUDY OVERVIEW

### 2.1.1 Study Duration

November 16, 1973 to February 15, 1975.

### 2.1.2 Study Objective

The study consisted of two tasks. Task I provided a broad picture of the kinds of flame retardants available, the extent of their use and the relative threat posed by the various technologies to the environment, the worker and the community.

Task II was an intensive study of the flame retardants for man-made fibers.

1. Halogenated polymers of textile polyesters, polyamides, and modacrylics.
2. Fibers containing coreactive and additive organophosphorus components, and similar aftertreatments for man-made fibers.
3. Aramids - fibers in which the fiber-forming substance is a long chain, synthetic polyamide with the amide linkages on two aromatic rings.
4. Other high temperature synthetic organic fibers.

Task II concentrated on the collection and analysis of information in the following areas:

1. Environmental fate, including
   a. biodegradation
   b. hydrolysis, oxidation, and other chemical processes occurring in the environment
   c. thermal decomposition
   d. radiation-induced changes
   e. bioaccumulation
   f. movement through the environment
2. Unreacted monomers and oligomers: levels in the finished fibers and their potential toxicity
3. Possible toxic (including environmental) effects from
   a. the polymers
   b. degradation products from the polymers
   c. waste products from production, fabrication, finishing, cleaning (including laundering), or use of the polymers or products containing the polymers
4. Uses and production levels, including trends and projections.

### 2.1.3 Study Methodology

In a two step process the study first established the state of the art with regard to chemical flame retardance, textile technology, government standards and economic pressures bearing on the industry. Step one highlighted the trends. Step two concentrated on the flame retardants most relevant to today's technology and looked beyond the obvious data directly related to textiles. It delved into the basic chemistry and biology of the modern flame retardants, their chemical families and related moieties in an attempt to identify potential problems that might be associated with their use.

Task I was basically an extensive literature search that resulted in retrieval of over 400 relevant articles. These were read, abstracted and analyzed and the results were submitted to EPA in April, 1974. Task II built on the literature based analysis of Task I. Additional subtasks consisted of:

- Consultation with acknowledged flame retardant specialists in research, industry and academia
- Additional primary references
- Unpublished reports of work in progress and proprietary reports and data sheets on specific products
- Government reports
- Current journal scan of scientific journals through February, 1975

Telephone conversations with executives of the man-made fiber industry and chemical industry proved helpful, particularly with regard to discussions of the market trends. Proprietary data on products in development or those that were semi commercial was not generally made available, however.

## 2.2 FINDINGS, CONCLUSIONS AND RECOMMENDATIONS

### 2.2.1 Nondurable Treatments

The role of the nondurable flame retardant formulations for use on textile materials is characterized by two factors: their total leachability and their low cost. The leachability severely limits their use in the growing market resulting from the Fabric Flammability Act of 1967; and, their low cost to achieve effective flame retardance assures their use in applications not subject to leachability. In the textile market this means they will become increasingly less important in any area covered by rigid standards. Draperies, bedding, plush toys and furnishings not covered by legislation will be the principal, but limited markets.

#### 2.2.1.1 Recommendation

In the course of this study, no reason for environmental concern was indicated with respect to the nondurable flame retardants. Ammonium phosphates, which are probably the most important ones still in use are of far greater concern, if indeed any is warranted, for their use,in nontextile markets than as textile flame retardants. No follow up investigation is recommended.

### 2.2.2 Durable Treatments

For treatment of cotton, rayon and to some extent the other natural fibers THPC and Pyrovatex™ (Ciba Geigy) are adequate to flame retard textiles. Pyrovatex™ has also shown promise as a finish for cotton/polyester blends. However, some growth markets are closed to them until they will consistently pass the leach requirements of 50 home launderings. Cotton's general loss of market position is the most significant factor likely to keep the use of durable cellulosic flame retardant treatments a limited specialty market. The treatments that will effectively treat the popular cotton/polyester blends may be entirely different chemically than those now in use for 100% cotton or 100% polyester.

As a known hazard, these flame retardant systems present only a minor occurrence of dermatitis. By-products of the manufacture and products of degeneration are more serious problems. In relation to the overall problems associated with disposal of textile mill wastes, the by-products of manufacture are unlikely to be significant.

### 2.2.2.1 Recommendations

Original investigation of the products of decomposition and interactions of the flame retardants with other chemicals commonly encountered in the textile industry should be undertaken. The special conditions under which THPC/OH systems might result in the generation of bis(chloromethyl) ether or other obnoxious products is the most important question requiring further investigation with regard to the durable flame retardants. An original investigation of the problem should be undertaken under the sponsorship of an appropriate Federal agency. Additional work to test the validity of Afanas'eva's work as reported in Section IV is also indicated as this search indicated there has been no follow-up study to date.

### 2.2.3 Man-Made Textiles

Despite petrochemical feedstock shortages, man-made textile fibers will continue to dominate the market. Of these, the cotton/polyester blends will be the most significant. For special flame retardant textile products such as apparel and both home and industrial furnishings, the market is predicted to expand from the current 5% level to 20% in 1980. Flame retarding techniques for textiles which will grow will be the use of coreactives, additives, and finishes; however, at this point, it is not predicted that any one of these will be of more significance than another. The next major technological growth area in textile flame retardant industry will be the flame retarding of blends. The techniques used for blends will be chemically different from those used either for 100% natural fibers or for 100% man-mades.

The flame retardants we studied, namely haloorganics, organic phosphates, aramids, and other high temperature polymeric structures, are all relatively stable in the environment. Very little information is available concerning their decomposition in sunlight, their thermal decomposition and combustion products, their biodegradation, or their solubility and solubility products [illegible] such matrices as human saliva, urine, sweat, or infantile bowel movements. Further, no long-term toxicity studies are available on these compounds.

Vinyl bromide is apparently increasing its share at the market. There is still insufficient published information to fully characterize its use and potential. Efforts to collect such information may require significant cooperation from the manufacturers.

### 2.2.3.1 Recommendations

We have found no evidence which would lead to exceptional environmental or toxic concern for the flame retardants for man-made textiles. Flame retardants used for non-textile purposes, or related chemicals used in fertilizers and pesticides would appear to be of more concern by virtue of their greater volume of use. However, continued monitoring of technological developments in this field are warrented. Specifically, we recommend that tests of these flame retardants and the chemicals with which they come into frequent contact be conducted. These would include chlorine bleach as well as the atmospheric components: ozone, sulfur dioxide, nitrous oxide, and cyanide. Of particular concern are circumstances under which the generation of analogs of bis chloromethyl ether might occur from interactions of chloride and bromide components of flame retardants with other fabric finishes. We further recommend legislation to require acute, subacute, and chronic toxicity testing as well as environmental monitoring of plant sites involved in manufacture or finishing, coupled with a mechanism for reporting of the results of these tests on a regular basis.

## SECTION III. NONDURABLE TREATMENTS

Nondurable flame retardant treatments are mixtures of chemical salts applied in a water solution to fabrics and end products that are not likely to be laundered or subjected to other water, such as perspiration or rain. Historically, nondurables are the oldest class of flame retardants. These water soluble treatments are easily applied, but just as easily leached out. Generally, they have to be reapplied after any substantial contact with water. Each of the general articles reviewed are similar in their discussions of the use of these treatments. Buck and Bhatnagar among others describe the formulations, uses and chemistry of these treatments in succinct but comprehensive fashion.[1,2] The definition of durability is a relative one. A nondurable treatment of a cotton or rayon batting with ammonium sulfamate used for insulation purposes and never exposed to water or leaching is, in a sense, durable. However, the common property of water solubility determines and limits the practical use of this class of flame retardants.

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[1] Buck, George S. Fire resistant textiles. In Encyclopedia of Chemical Technology, 1st, Interscience Encyclopedia, N.Y., 1951, 6, 543-558 (OTS-AA-0339).

[2] Bhatnagar, Vijay M. Fire retardant formulations handbook. Westport, Conn. Technomic, (1972) (OTS-AA-0010).

## 3.1 NONDURABLE FORMULATIONS

The list of inorganic compounds that have been used at one time or another as nondurable flame retardants is quite extensive. A select list of the more effective compounds still in use is shown in Table 3-1. Their relative effectiveness is indicated by the percent add-on necessary to prevent flaming.[3]

The more common treatments are usually synergistic mixtures of two or more salts which are more effective than either component alone. Formulations that have been reported in two or more sources to be useful for textiles are:

- seven parts borax, three parts boric acid;
- seven parts borax, three parts boric acid, five parts diammonium phosphate;
- one part sodium phosphate, one part borax, one part boric acid, one part diammonium phosphate;
- ten parts borax, seven parts boric acid, three parts sodium phosphate;
- ammonium sulfamate alone;
- three parts ammonium sulfamate, one part diammonium phosphate;
- ammonium bromide alone;
- 15 parts borax, 47 parts boric acid, 18 parts sodium phosphate, 20 parts sodium tungstate.

## 3.2 PHYSICAL PROPERTIES

Water solubility is the outstanding physical characteristic common to the nondurable flame retardants. In addition to the relative inflammability of the compounds shown in Table 2-1, the effective treatments exhibit synergistic properties in mixtures. For example, an add-on of 60% of borax is required to prevent fabric flaming, and boric acid by itself is inefficient as a flame retardant even with an add-on level of 300% by weight. A mixture of seven parts

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[3] Buck, George S. op. cit.

## TABLE 3-1. AMOUNT OF RETARDANT REQUIRED TO PREVENT FLAMING AND GLOWING (NONDURABLE FINISHES)

| Retardant | Minimum add-on, %* |
|---|---|
| Ammonium bromide, $NH_4Br$ | 7 |
| Ammonium molybdate, $(NH_4)_2MoO_4$ | 7 |
| Sodium tungstate, $Na_2WO_4.2H_2O$ | 9 |
| Diammonium phosphate, $(NH_4)_2\ HPO_4$ | 12 |
| Phosphoric acid, $H_3PO_4$ | 12 |
| Zinc chloride, $ZnCl_2$ | 12 |
| Ammonium iodide, $NH_4I$ | 14 |
| Calcium chloride, $CaCl_2.6H_2O$ | 14 |
| Magnesium chloride, $MgCl_2$ | 16 |
| Ammonium sulfate, $(NH_4)_2SO_4$ | 18 |
| Sodium stannate, $Na_2SnO_3$ | 18 |
| Sodium aluminate, $NaAlO_2$ | 19 |
| Sodium silicate, $Na_2SiO_3.9H_2O$ | 20 |
| Ammonium chloride, $NH_4Cl$ | 22 |
| Ammonium borate, $NH_4BO_3$ | 24 |
| Sodium bisulfate, $NaHSO_4.H_2O$ | 30 |
| Sodium arsenate, $Na_3AsO_4.12H_2O$ | 33 |
| Borax, $Na_2B_4O_7.10H_2O$ | 60 |

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* Parts by weight added per 100 parts fabric.

borax and three parts boric acid on the other hand, gives adequate flame retardance with only 6 1/2% add-on.[4]

Nondurable treatments possess the properties that would make them very desirable as flame retardants for many textile uses, if it were not for their water solubility. They add little to the fabric weight. They usually do not affect the color or tensile strength of the fabric. When carefully applied, the small add-on required for the more effective treatments has little effect on the hand, drape, flexibility, and tear strength of the treated fabrics. Regardless of the various demands for different finishing properties, combinations and modified formulations can be made to meet specified requirements. Some formulations may cause cloth stiffening, as the stiffening effect of the various salts and mixtures varies considerably.[5]

The nondurable flame retardants act by a combination of mechanisms. Some form a foam coating of fused particles that protects the fabric from further combustion. They also release mineral acids that alter the cellulose degradation mechanism. They can also snuff out a flame by generating a noncombustible atmosphere of gases and vapors. The natural action of inorganic salts to lower the decomposition point of the cellulose polymer is sufficient, in some cases, to cause gradual yellowing and loss of tear strength in treated fabrics if they are subjected to drying or prolonged heating in application processes. Although at ordinary temperatures no appreciable deterioration of finished fabrics is likely to occur with any of the treatments, exposure to sunlight or elevated temperatures will, in most cases, cause a considerable loss in strength. The significance of this phenomenon is that the use of such treatments on materials such as curtains, home and office furnishings and automobile carpets and upholstery exposed behind windows in direct sunlight would be destructive to cellulosic fabrics.

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[4] Kasem, M. Abul; M. Richards. Flame-retardants for fabrics. Function of boron-containing additives. Industrial & Engineering Chemistry, Product Research & Development, 11 (2): 114-33, (1972). (OTS-AA-0048).

[5] Smith, James Kenneth, et al. Thermochemical investigation of cotton flame retardance. Textile Research Journal, 40 (3): 211-16, (1970). (OTS-AA-0092).

In the mixtures of salts chosen for flame retardant formulations, early workers with nondurable treatments looked for deposits which would not crystallize on the fabric as an important physical characteristic. Not only would crystallization have caused aesthetic problems, but it tends to inhibit the flame retardant properties of the mixtures. Thus, the nondurable treatments currently in use do not crystallize on treated fabrics.

Lyons provides some comparative flame retardance data on seven nondurable formulations studied for their effect on cotton fibers.[6] Table 3-2 shows the data collected on the test formulations at a 10% add-on after the vertical flame test method. The inferior position of ammonium sulfamate ($NH_4SO_3NH_2$) compared to the ammonium phosphates is clear. Afterglow with boron-treated compounds is also seen as a problem, but they seem to display a superior performance with lower char lengths than the other retardants. In several similar tests involving more durable phosphate containing retardants, the glowproofing superiority of phosphorus-containing flame retardants is further supported.[6]

## 3.3 ECONOMIC CONSIDERATIONS

The principal advantage of the nondurable treatments has always been their relative low cost. Before the current inflationary period, the nondurable finishes that were easily applied in a commercial laundry with a 10-15% dry add-on in a simple pad-dry operation could be produced at approximately 20 cents per pound of chemical, or approximately 2-3 cents per pound of cotton treated. This cost was roughly the same for any of the more common formulations described in section 2.1, preceding. For example, an 8 ounce per square yard fabric would cost an additional 1 to 1.5 cents per square yard. If the pad-dry operation costs 2 cents per yard, the final cost at the mill was 3 to 3.5 cents per yard of fabric for fire retardance, compared to a cost of 13 to 15 cents per square yard for cotton treated by one of the more durable processes. However,

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[6] Lyons, John W. The chemistry and uses of fire retardants. New York, Wiley-Interscience, 1970. (OTS-AA-0075).

## TABLE 3-2. VERTICAL FLAME TEST RESULTS OF NONDURABLE TREATMENTS[1]

| Treatment | Afterglow, Sec. | Char length, in. |
|---|---|---|
| Borax: Boric Acid (7:3) | 190 | 2.6 |
| Borax: Boric Acid (1:1) | 32 | 2.7 |
| $(NH_4)_2HPO_4$ | 0 | 3.9 |
| $NH_4H_2PO_4$ | 0 | 3.4 |
| Borax: Boric Acid: $(NH_4)_2HPO_4$ (7:3:5) | 8 | 3.2 |
| Borax: Boric Acid: $(NH_4)_2HPO_4$ (5:5:1) | 43 | 3.1 |
| $NH_4SO_3NH_2$ | 550 | 5.0 |

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[1] Source: Lyons, John W. (see note 6, p. 3-5)

for a hospital or institutions where continual reprocessing was needed, the costs are additive.[7,8,9]

The additive costs for reprocessing institutional materials has increasingly reduced the economic advantage of the nondurables, and, with the development of inherently flame retardant fabrics of man-made fibers, institutional use of nondurable flame retardants has virtually been eliminated.[7,9,10]

No data were found to identify the economic forces affecting the individual submarkets of the specific nondurable treatments. In most instances, it was not possible to identify the textile flame retardant markets for the chemicals involved in nondurable treatments, since these are overshadowed by the wide and varied uses of the chemical compounds involved. Monoammonium phosphate and diammonium phosphate, for example, are probably the most heavily used nondurable textile flame retardants currently employed; however, these compounds are even more commonly used in agricultural feeds and fertilizers, and their market as flame retardants is relatively insignificant.

### 3.3.1 Producers and Production

Table 3-3 lists the major suppliers of inorganic salts for flame retardants. The extent to which these suppliers are responsible for textile flame retardant formulations is not differentiated from their supplying the same chemicals for other uses. Nor is the use for nondurable treatments differentiated from use in durable formulations.

Production figures related to fire retardant textiles are not clear. Ammonium phosphate, ammonium sulfamate, borax, boric acid, ammonium chloride and ammonium bromide are probably the salts used more than any others. Figures on their actual use as textile flame retardant treatments is clouded by their

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[7] Title, M. M.; M. S. Brent. Purchasing flameproof fabrics that meet the fire code. Part 2. Hospital Management, 94, 73-6 (1962). (OTS-AA-0366).

[8] Gardner, H.K.; et al. Applying a durable flame retardant with inplant equipment. Hospitals, 37, 123-6, (1963), 16 Nov. 63. (OTS-AA-0369).

[9] Title, Monroe M.; M. S. Brent. Purchasing flameproof fabrics that meet the fire code. Hospital Management, 94, 74-6, (1962). (OTS-AA-0398).

[10] Jacobs, E. A.; et al. Testing flame retardant linen for hospital use. Hospitals, 42, 65-7, 144, (1968), 16 May 68. (OTS-AA-0372).

## TABLE 3-3. SUPPLIERS OF FLAME RETARDANT SALTS[1]

| Company and Treatment | Chemical |
|---|---|
| American Cyanamid | |
| Aerotex Fire Retardants | Inorganic Salts |
| Dexter Chemical | |
| Protonoc | Inorganic Salts |
| DuPont | |
| CM and X-12 Flame Retardants | Ammonium Sulfamate |
| Freeport Kaolin | |
| PA 1 | Aluminum Phosphate |
| GAF | |
| Gaftex Fire Retardant | Inorganic Salts |
| Great Lakes | Ammonium Bromide |
| Humphrey Chemical | |
| ZB | Zinc Borates |
| HFX-500 | Proprietary |
| Laurel Products | |
| Pyrosan | Inorganic Salts |
| March Chemical | |
| Flame-Safe | Fusable Salts |
| Monsanto | |
| Phos-Chek | Ammonium Phosphates |
| Scholler Brothers | |
| BR Salts FP-SP | Inorganic Salts |
| Selig Chemical | |
| Flammex | Inorganic Salts |
| Sun Chemical | |
| Warconyl 351-A | Inorganic Salts |
| Swift & Co. | |
| Brominex | Proprietary |
| Charles S. Tanner | |
| CST Fire Retardant | Inorganic Salts |
| Tanotard | Organic and Inorganic Salts |
| U.S. Oil | |
| Usco Fire Retardants | Inorganic Salts |
| U.S. Borax | Borax, Boric Acid |
| FR-28 | Sodium Borate |
| Firebrake 2B | Zinc Borate |

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[1] Source: American Dyestuff Reporter, January and February 1972.

use as feedstocks for the production of other flame retarded materials, particularly halogenated polymers and phosphate polymers for nontextile products.

Estimates on the use of ammonium phosphates consumed as cellulosic fire retardants, including paper and wood products, put consumption at about 18 thousand short tons per year. Monsanto is the principal supplier with over two thirds of the market. The primary competitive material in cellulosic fire retardation is DuPont's ammonium sulfamate. The products apparently compete equally on a price basis. As noted previously, ammonium phosphates are more effective, but ammonium sulfamate is reported to be less of a skin irritant.

The relatively minor role of inorganic salts used as flame retardants is demonstrated by Monsanto's production figures for 1973. Monsanto's production capacity for monammonium phosphates and diammonium phosphate together is approximately 45 thousand short tons. Its principal market consumption is estimated as:

| | |
|---|---|
| Fertilizers | 5,071 short tons |
| Livestock feed | 37 short tons |
| Fire Control | 45 short tons |
| extinguishers | 17 short tons |
| flame retardants | 18 short tons |
| forest fire control | 10 short tons |
| Other | 11 short tons |
| Total | 5,164 short tons |

### 3.3.2 Principal Markets and Uses

The use of nondurable flame retardants has steadily declined since the late 1950's when practical, durable treatments for cellulosic materials began to become available on a commercial bases. Institutional uses at hospitals, particularly those of the Veteran's Administration, provided the bulk of the market for nondurable flame retardants until that time. A smaller, yet significant market was also maintained in such industries as steel where exposure to flame was an occupational hazard. In such applications, which existed in highly controlled environments, it was possible to reapply a flame retardant finish to the fabric after each use. Curtains and drapes in theaters and other public buildings provided another popular market for the nondurable formulations.

Current nondurable flame retardant markets are largely for uses not covered by federal legislation. Many of the products are applied in the last rinse water at industrial and commercial laundries, where their uses are still found economical either because of limited use, or to avoid a major capital reinvestment. Building materials, drapes, tapestries and the like are flame retarded with a spray application. In these and other uses, the market is not readily definable. Additional, contemporary market consumption patterns that have been suggested are for cotton flote products, or the plush toy market where there is not yet any strong legislation, but the manufacturers involved are concerned about product liability as well as attempting to prevent the kinds of fire incidents that would lead to legislative controls.[11]

The market position of the nondurable flame retardant treatments is directly linked to the overall textile market. Nondurable treatments are effective on cellulosic fabric. The cellulosic textiles are not only losing market position in general to the man-made fibers, but they are losing out specifically in the area of flame retardant products since the standards set to determine flammability include a leaching procedure that for most of the products eliminate the water soluble treatments before testing. In addition, it seems that even if the current standards were modified to permit the use of less than permanently durable flame retardants in products such as carpets or upholstery, when those products are covered by legislation, the treatments that are likely to benefit are semidurable combinations rather than the truly nondurable treatments here.[12,13]

For all practical purposes, it appears from the current market trends that the inorganic salts applied to cellulosic textiles, primarily cotton, are less desirable than a range of other phosphorus and nonphosphorus chemical compounds for fire retardant treatments. Market growth expected as a result of recent legislation is shown in Table 3-4. Of the seven major markets that are likely to be the controlling factors in the growth of flame retardants, nondurable treatments are apt to benefit mostly from nontextile applications. Carpet and rug standards (DOC FF-1-70, FF-2-70) require ten scrubbings, apparel standards, 50 washings. In these products nondurable treatments will find no market. Bedding standards (FF-4-72) have reduced or eliminated the leaching procedure and may provide some market for the nondurables in the padding. However, the full impact on the bedding industry and its response is not yet complete. Industry spokesmen refer to a need to totally redesign bedding in response to federal standards. Factors such as the tightness of weave, the use of nonflammable thread, the design of gatherings at the edges and corners and the choice of component materials may be more significant than flame retardant treatments of the textile component.[14] It seems unlikely that the forthcoming standards on upholstery and other home furnishings are likely to be less stringent than the carpeting standards.

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[11] Refer to note 9, page 3-7.

[12] Friedman, M.; R.E: Whitfield, S. Tillin. Enhancement of the natural flame-resistance of wool. Textile Research Journal, 43 (4): 212-17, (1973) (OTS-AA-0039).

[13] Gilbert, S.; R. Liepins. Treatment for improving flame retardancy of wool and minimizing toxic gas evolution in burning. Journal of Applied Polymer Science, 16 (4): 1009-16, (1972) (OTS-AA-0040).

Anticipated growth is seen more directly linked to uses in paper and wood products, and in some internal insulation materials used in construction. Paper products including facial tissue, boxboard, decorative paper, insulating board, book matches and cigarette papers are more promising markets for the nondurables than textile products. Ammonium phosphates are consumed as flame retardants on cellulose construction products such as beams, insulation, ceilings, chipboard and siding used for internal construction.

Forest fire control and fire extinguisants are further areas of growth that are more probably going to receive the impetus of marketing efforts by the major producers than are nondurable textile treatments. Solid ammonium phosphate is the leading chemical used as an active ingredient in these solutions with 45-55% of the total market volume. Ammonium sulfate represents about 30% with the rest going to ammonium polyphosphate solutions.

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[14] Roe, Richard C. The impact of the new federal flammability standards on the bedding industry. ASTM Standardization News, 1 (5): 23-25, (1973) (OTS-AA-0402).

## TABLE 3-4. FLAME RETARDANT MARKETS[1]

| Market | Estimated Consumption (Millions of pounds per year) | |
|---|---|---|
| | 1971 | 1975 |
| Carpets and rugs | 100-125 | 425-550 |
| Construction | 14-22 | 75-100 |
| Miscellaneous nondurables* | 10-15 | 15-20 |
| Electrical and electronics | 11-12 | 35-40 |
| Apparel | 8-10 | 34-36 |
| Transportation | 4-5 | 70-80 |
| Home furnishings | 3-4 | 20-25 |
| Total | 150-193 | 674-851 |

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*wood, paper and other nondurables

[1] Source: Chemical and Eng. News Oct. 18, 1971 (OTS-AA-1346)

### 3.3.3 Transportation

The transportation patterns for flame retardant materials either as preprocessing chemicals or finished goods was not discernable from the data reviewed. It does appear that the inorganic materials listed in Table 3-3 are provided to the textile mills in powder form. Ammonium phosphates, ammonium sulfamate, ammonium halides and borax are transported interstate by rail and truck. Domestic producers probably account for all the bulk chemicals used in the nondurable flame retardant textile formulations and products. Imports do not appear to have a significant role other than the supply of raw textile materials.

## 3.4 ENVIRONMENTAL IMPLICATIONS

The textile finishes described in this section involve chemical compounds that in large supply could bring with them several environmental hazards. Air and water pollution by the raw chemicals involved could conceivably result in corrosion and toxicity problems. However, the use of phosphates, ammonium sulfamate, borax, boric acid, and ammonium halides as textile flame retardants is virtually insignificant compared to their use in agriculture, other chemical processes and even as flame retardants for nontextile, cellulosic materials. The environmental implications resulting from their use as textile flame retardants are thus of minor import compared to their contribution to environmental hazards from their use in other capacities.[15]

### 3.4.1 Contamination

The data reviewed do not indicate that the use of inorganic salts *per se* as textile flame retardants is a source of environmental contamination. Handbooks, industrial hygiene texts, and journal data covering air, soil and especially water pollutants emanating from textile mills, at best make reference to the general problems of inorganic salts as a water pollutant.[16,17,18] The potential contaminants are limited principally to the phosphates as water pollutants, escaping ammonia from the drying processes that is ventiliated into the environs of the finishing mills, and hydrogen chloride and hydrogen bromide generated in a fire by the ammonium halides.

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[15] Burr, Francis K. Textile Waste Treatment. In Kirk Othmer Encyclopedia of Chemical Technology. (supplement) Wiley-Interscience, N.Y., 1971, 979-983 (OTS-AA-0370).

In the drying processes, the ammonium compounds tend to give off ammonia gas through decomposition. Diammonium phosphate, in particular, loses ammonia and is converted to monoammonium phosphate at a rate directly proportional to temperature increases. This reaction reportedly can proceed with only sunlight as an energy source. At 125°, monoammonium phosphate is stable, but diammonium phosphate is not. This is described by Lyons[19] according to the following equation:

$$NH_4\ H_2\ PO_4 \rightleftharpoons NH_3 + H_3\ PO_4$$

$$\mathrm{Pmm} = 0.05 \text{ at } 125^{\circ}C$$

$$(NH_4)_2\ H\ PO_4 \rightleftharpoons NH_4\ H_2\ PO_4 + NH_3$$

$$\log \mathrm{Pmm} = \frac{3063}{T} + 1.75 \log T + 3.3$$

where: P = millimeters of Hg.
T = absolute temperature in degrees Kelvin.

Documentation of phosphate pollution of water is quite extensive and beyond the scope of this present volume. An indication of several of the significant problems that would be exacerbated by the extensive use of ammonium phosphates as nondurable flame retardants is provided in a symposium entitled "Phosphorus in Fresh Water and the Marine Environment", published in Water Research 7 1/2 1973. However, serious consideration of this problem as a result of the increasing use of these compounds as flame retardants for nontextile cellulosic products might be a proper study beyond the present one.

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[16] Mark, H.; S.M. Atlas. Environmental hazards of modern textile finishing. In: H. Mark chemical After-treatment of textiles. Interscience, N.Y., 1971, 631-4 (OTS-AA-0348).

[17] Anonymous. Textile waste cleanup. Environmental Science and Technology, 7(8): 682-683, (1973) (OTS-AA-0383).

[18] Trobisch, K. Measures against water pollution in industries producing petrochemicals including polymers. Pure and Applied Chemistry, 29 (1): 57-65, (1972) (OTS-AA-03[illegible])

[19] Refer to note 6 on page 3-5.

Monitoring and analysis of nondurable flame retardants is a poorly documented field. The common chemicals used have been analyzed by both spectroscopic and chromatographic methods. General analytical data is readily available in the standard handbooks of the appropriate fields. One newer technique specific to the present discussion was retrieved.[20] Elliott, Heathcote and Mostyn report on a procedure for the determination of phosphorus in fire resistant textiles by cool flame emission spectroscopy. Basically, they show that this technique is suitable only for nondurable treatments. Residual acids as nitrates and sulfates present in extracts with the durable finishes interfere with the interpretation of data on the durable finishes. A complete determination by this method requires about four hours, with an ion exchange stage accounting for over one half of the overall time.

### 3.4.2 Biology and Toxicity

Borax-boric acid mixtures are the least hazardous components of the nondurable flame retardant formulations. In a German study, the boric acid concentration was measured in the blood of 21 hospitalized patients treated with wet compresses over several days. Only one patient showed a significant rise. There were indications that pre-existing kidney damage was responsible. Follow up studies on rabbits with kidney damage indicated that the half time value of boric acid in the blood was significantly prolonged. In the diseased state, the toxic limit in the blood was easily reached through bioaccumulation.[21] By analogy, it may be valid to speculate that flame retardant salts would exhibit the same results. Again, the reduced use of these materials in hospitals, in particular, limits the significance of these findings for the nondurable treatments, but raises it where bedding is still so treated.

The biological implications of the nondurables are again characterized by their solubility. Any skin contact creates a potential for immediate absorption. Toxicity is generally low. Ammonium sulfamate is sold under the name "Ammate" as a weed killer and reportedly has an oral $LD_{50}$ in rats of 3.9 g/kg. Although similar data were not obtained for the other major compounds, ammonium phosphates can cause skin irritations more readily than ammonium sulfamate. The ammonium halides are both more active. Ammonium chloride is used as an expectorant and is a diuretic for human and veterinary purposes. It has an intramuscular $LD_{50}$ in rats of 30mg/kg. Ammonium chloride is known to cause pulmonary edema in humans, cats and guinea pigs.[22,23] Ammonium bromide is a sedative at an oral dose of 0.6 to 2g. Gastrointestinal distrubances have been reported as side effects.

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[20] Elliot, W.N.; C. Heathcote, R.A. Mostyn. Determination of phosphorus in fire-resistant textiles by cool-flame emission spectroscopy. Textile Research Journal, 42 (2): 86-8, (1972) (OTS-AA-0035).

[21] Schuppli, R.; et al. On the toxicity of boric acid. Dermatologica, 143 (4): 227-234, (1971) (OTS-AA-0354).

## 3.5 SUMMARY AND CONCLUSIONS

The role of the nondurables in the overall flame retardant picture is characterized by two factors: their total leachability and their low cost. The leachability severely limits their use in the growing market resulting from the Fabric Flammability Act of 1967; and, their low cost to achieve effective flame retardance assures their use in applications not subject to leachability. In the textile market this means they will become increasingly less important in any area covered by rigid standards. Draperies, bedding, plusn toys and furnishings not covered by legislation will be the principal, but limited markets.

The effective combinations and formulas have been fully developed. With no need for further development, the compounds discussed in section 3.1 will constitute the basic ingredients of formulations that could find use in future markets. These compounds are relatively innocuous, particularly since they will not be used to the extent that strong concentrations are likely to result except in the immediate processing areas of a textile finishing mill.

Additional data that might be developed from an intensive study of nondurable textile flame retardant formulations would be germane, but dated.

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[22] Nitta, Sumio; N.C. Staub. Lung fluids in acute ammonium chloride toxicity and edema in cats and guinea pigs. American Journal of Physiology, 224 (3): 613-617, (1973) (OTS-AA-0360).

[23] Szam, Istvan; E. Vincze, J. Szentner. The pathogenesis of ammonium chloride pulmonary edema. Zeitschrift füer die Gaesamte Innere Medizin und ihre Grenzgebiete, 26 (12): 378-383, illus., (1971) (OTS-AA-0350).

The most significant, contemporary data that might be developed in addition to this volume, is a detailed characterization of the nonlegislated uses of the nondurable treatments, but such data is not readily available, and of minor importance both from the point of view of volume of use and potential hazard.

# SECTION IV. DURABLE AND SEMIDURABLE TREATMENTS

Durability is a relative concept relating to the ability of a flame retardant chemical system for textile materials to withstand water and washing to some degree. Although most authors on flame retardants for textiles differentiate between the two classes, both the semidurable and durable treatments are intended for use on products that will retain their flame retardance for the useful life of the product under normal circumstances. The semidurable treatments have little or no resistance to dry cleaning solutions and will not withstand more than a few launderings. The loss of flame retardance for both durable and semidurable treatments depends on the progressive leaching of the flame retardant, and ion exchange aggravated by the ionic contents of hard water and/or deposition of insoluble carbonate precipatates on the fabric. Chlorine bleaching, weathering and sun exposure are also antagonists to durable treatments. The relative resistance of the various flame retardant systems determines their ultimate "durability".

In the context of the literature of textile finishing, the terms durable and semidurable generally have been applied to cotton and rayon finishing. Wool, silk and other natural fibers have also been treated by modified systems based on those developed for cellulosics. As such, this section is concerned with treatments of cellulosics, especially cotton, and includes references to the other natural fibers. Discussion of durable treatments of man-made fibers and end products is reserved for Section V.

## 4.1 SEMIDURABLE AND DURABLE FORMULATIONS

### 4.1.1 Semidurable Flame Retardant Treatments

In an effort to improve the resistance of flame retardant treatments to leaching and laundering, various inorganic materials have been used in a variety of systems. Metal oxides precipitated in cotton fabric were an early example of these attempts. Titanyl chloride and zinc compounds proved to be somewhat effective, but only in combination with other flame retardants. None of these flame retardants has found any commercial success to date and are chemical curiosities more than anything else. However, the natural flame retardant properties of several metal salts have been found to add to the inherent flame retardance of wool when employed as mordants.[1,2,3]

Cellulose phosphate esters formed by direct esterification of the cellulose molecule with phosphoric acid have provided systems with some commercial success. The most successful approaches have employed a urea-phosphate treatment and a melamine-formaldehyde-phosphate system. Other nitrogen bases have been substituted for the urea on an experimental basis including guanidine, ammonium

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[1] Benisek, L. New aspects of flame protection using wool: versatile, simple, inexpensive. Internat. Dyer Textile Printer Bleacher & Finisher, 147 (7): 414-16, 418-19, (1972) (OTS-AA-0008).

[2] Refer to note 12, Section III, page 3-10.

[3] Benisek, L. Use of titanium complexes to improve the natural flame retardancy of wool. Journal of the Society of Dyers & Colourists, 87 (8): 277-8, (1971) (OTS-AA-0146).

sulfamate and cyanamide. The cyanamide-phosphoric acid process has been refined by O'Brien and is the basis of Pyroset, an American Cyanamid proprietary process.[4,5,6,7]

The cyanamide-phosphoric acid formulation is applied by the pad-dry-cure technique using a formulation of three parts cyanamide to one part phosphoric acid. Durability to laundering is limited to five to ten home launderings. Loss of the resin and the precipitation of sodium phosphates as a result of ion exchange antagonize the flame retardance.

Chlorinated paraffin wax (40 to 70% chlorine) with antimony oxide and stabilizers have been used widely in outdoor military applications since World War II. Chlorinated paraffin wax is the actual flame retardant in the formulations. The antimony oxide is added for its effectiveness as an afterglow inhibitor. A ratio of approximately 1·1 is most effective. Several mixtures are described by Bhatnagar.[8] The formulations are prepared by techniques used for paints. The solids are ground in the presence of the resins or chlorinated paraffin wax and then diluted to an appropriate consistency with organic solvents. The fabrics are saturated and squeezed through padded rollers to remove the excess material, and dried. Curing is not required. Other chlorocarbons have been used in place of the chlorinated paraffin waxes. Latex resins of vinyl chloride containing polymers, polyvinyl chloride, and chlorinated rubber have been reported to be successful replacements.

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[4] Kovacs, J.; C.S. Marvel. Synthesis of 1,4,5,6,7,7-hexachloro- and hexabromobicyclo-(2,2,1)-5-heptene-2carboxylic acid vinyl esters and copolymerization with acrylonitrile. Journal of Polymer Science, Part A-1, 5 (6): 1279-87, (1967) (OTS-AA-0055).

[5] Krackeler, Joseph J.; D. Hoogensen. Halogenated hydrocarbons flame retard polyurethanes. Rubber World, 163 (2): 53-7, (1970) (OTS-AA-0056).

[6] Lam, L.K.M.; et al. Identification of cis-4,5-epoxy-2-pentenal from pyrolysis of phosphoric acid treated cellulose. Journal of Applied Polymer Science, 17 (2): 391-9, (1973) (OTS-AA-0057).

[7] O'Brien, S. James; R.G. Weyker. Application of Pyroset CP flame retardant to wool. Textile Chemist & Colorist, 3 (8): 185-8, (1971) (OTS-AA-0155).

[8] Refer to note 2, Section III, page 3-1.

### 4.1.2 Durable Flame Retardant Treatments

Esters of phosphonoalkanoicamides and several variations of treatments based on tetrakis (hydroxymethyl) phosphonium compounds now dominate the flame retardant finishing of cotton fabrics.

Ciba-Geigy's Pyrovatex FR is a treatment based on N-methylol dimethyl phosphonopropionamide. The compound is padded on the fabric by the conventional pad-dry-cure procedures. The treated fabric is dried and cured for one to two minutes at 175°.[9,10] Commercially, it is used with a triazine resin, a surfactant, urea, polyethylene softener, and ammonium chloride.

The treatments based on tetrakis (hydroxmyethyl) phosphonium compounds are derived from tetrakis (hydroxymethyl) phosphonium chloride (THPC). THPC can be reacted with sodium hydroxide on a 1:1 basis to produce tetrakis (hydroxymethyl) phosphonium hydroxide (THPOH) which provides a series of variant treatments. The important THPC/OH systems that are in use are as follows:

THPC, methylol melamine, urea, heat

THPC, methylol melamine, urea, partial heat cure, partial $NH_3$ cure

THPC & tris(l-aziridinyl)phosphine oxide with heat

THPC + NaOH, methylol melamine, urea, heat

THPC + NaOH, amide, partial heat cure, partial $NH_3$ cure

THPC + NaOH, methylol melamine, urea, copper

THPC + NaOh, $NH_3$ cure

The significance of textile flame retardance as a chemical system is incisively shown by the numbers and nature of the performance variations possible with just a few basic compounds and technical processing modifications. Beninate

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[9] Aenishanslin, R.; et al. A new chemical approach to durable flame retardant cotton fabrics. Textile Research Journal, 39 (9): 375-381, (1969) (OTS-AA-0001).

[10] Drake, George L., Jr. Flame resistant and rot resistant finishes: application to cellulose. American Dyestuff Reporter, 56 (15): 560-4, (1967) (OTS-AA-0125).

compares several curing techniques and demonstrates that the THPOH-ammonia cure process, which is the newest development, not only has greater durability and results in a relatively good fabric condition, but simplifies the processing while making it less hazardous through eliminating the need for gaseous ammonia as a reactant.[11,12]

A number of flame retardant compounds have been synthesized from specific amine-phosphorus reactions in addition to those already discussed. A great interest has been shown in reaction products of $POCl_3$ and $NH_3$ in particular. Only one compound has gone beyond the research stage. Tris(1-aziridinyl) phosphine oxide, the reaction product of ethyleneimine and phosphoryl trichloride, has been used commercially, but it has not been as successful as originally anticipated. Toxicity with the unreacted monomer has severely limited its use. Dow Chemical, the major producer, has reportedly discontinued its manufacture.[13] Efficacy and durability tests have been encouraging, however.[14]

## 4.2 PHYSICAL PROPERTIES

### 4.2.1 Physical Characteristics of Semidurable Treatments

The cellulose phosphate esters produce finishes that have little effect on the hand of the fabric. The treated finishes are physically stable and they also provide rot and crease resistance. The urea-phosphate treatment degrades the cellulose. Tensile strength is lost depending on the amount of urea present in treatment. Normal tensile strength loss is 35 to 45%. However, excess urea is needed to resist ion exchange. Commercially, cyanamide has been used in place of some of the urea. Even in formulations where cyanamide is used in place of 75% of the urea, tensile strength loss is still significant. The susceptability of the cellulose phosphate esters to ion exchange, which

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[11] Beninate, John V., et al. Application of a new phosphonium flame retardant. American Dyestuff Reporter, 57 (25): 981-985, (1968) (OTS-AA-0144).

[12] Beninate, John V., et al. Economical durable flame-retardant finish for cotton. Textile Research Journal, 39 (4): 368-74, (1969) (OTS-AA-0145

[13] Refer to note 6, Section III, page 3-5.

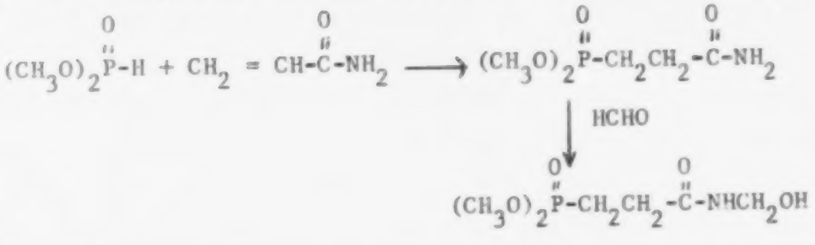
[14] Drake op. cit.

reduces the flame retardance of this combination, is the characteristic that most limits its utility. The ammonium ions in the compound are gradually replaced with sodium. When this happens, the fabrics burn, although the basic ester group is still present. The reaction is reversible, and flame retardance can be restored with a treatment of an acid, followed by a water solution of ammonium hydroxide. The treatment is unsuited for products that might be subjected to home laundering.

Chlorinated paraffin wax-antimony oxide formulations produce finishes that are durable to water leaching, but are readily removed by hot water, alkaline laundering. The fabrics tend to have a heavy, greasy hand, poor drape, and are difficult to dye. The flame retardance effectiveness is attributed to the thermal stability of the paraffin wax or other chlorocarbons that might be used. The mechanism of action is related to the creation of hydrogen chloride in combustion. The antimony oxide acts as a glow inhibitor. Modern preparations involving oil in water and water in oil emulsion systems have been developed to replace the use of the highly flammable and toxic solvents originally used in the manufacture of these flame retardant treatments.[15]

## 4.2.2 Physical Characteristics of Durable Treatments

Pyrovatex is an ester generated as a reaction product of a dialkyl phosphite and acrylamide.[16] The compound is a methylolated derivative with one mole of formaldehyde to one mole of the dialkyl phosphonopropionamide:



$$(CH_3O)_2\overset{O}{\overset{\|}{P}}\text{-}H + CH_2 = CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \longrightarrow (CH_3O)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow{HCHO} (CH_3O)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}NHCH_2OH$$

Excess formaldehyde in the process is released during fabric processing and the subsequent use of an acid catalyst causes a reaction with cotton. Efficacy and durability are added to the finish through use of an appropriate crosslinking agent, trimethylolmelamine, for example. Ciba-Geigy publications claim the finished product is nonirritating to the skin and produces a soft to slightly full hand. About 25% tensile strength loss is reported, which is more than that experienced with the THPC-ammonia finish,[17] Add-ons for cotton textiles are about 20-35% to produce effective flame retardance.

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[15] Ranney, Maurice W. Flame retardant textiles. Noyes Data Corp., Park Ridge, N.J., 1970, 373pp. (OTS-AA-0207).

[16] Refer to note 9 page 4-4.

THPC was first reported by Hoffman in 1921.[18] It is a crystalline compound that is readily soluble in water. It is produced in high yield through the reversible reaction of formaldehyde with phosphine and hydrogen chloride:

$$PH_3 + HCl + 4\ CH_2\ O \longrightarrow ((HOCH_2)_4P)\ Cl$$

Curing is accomplished by reacting the tetrakis (hydroxymethyl) phosphine (THP) group with an amine, involving aminized cotton or a suitable curing agent. The methylol groups react with the amino groups:

$$(HOCH_2)_4PCl + RNH_2 \longrightarrow RNHCH_2PCl(CH_2OH)_3 + H_2O$$

and $RNHCH_2$ replaces some methylol groups, the chlorine is hydrolyzed and the reaction proceeds:

$$(RNHCH_2)_3\ (CH_2OH)PCl + H_2O \longrightarrow HCl + CH_3OH + (RNHCH_2)_3PO$$

The finish contains no chlorine and the phosphorus is a true phosphine oxide, the most stable phosphorus state with regard to hydrolysis. The generation of HCl and formaldehyde in curing THPC is the most significant technical problem with THPC based systems. Formulations to replace the chloride use sodium hydroxide which does not yield the phosphonium hydroxide, per se, but rather a mixture of phosphines and phosphine oxides.[19,20,21] The THPC/OH systems have removed the HCl by-products from the process and they make less probable the release of formaldehyde on curing. In the most recently developed formulations, THPOH-trimethylolmelamine-ammonia and THPOH-amide, 1 mole of THPC is reacted with one mole of NaOH and the NaCl is removed by filtration from a methanol-water solvent. The other ingredients are added to the solution, the fabric is padded, dried and cured by gaseous ammonia or by heating at 150°. The fabric has excellent durability to laundering, and has passed the test for children's sleepwear after 50 launderings. It gives char lengths in the range of 2.5-4.5 inches. The product is a wash and wear fabric with permanent press properties and is resistant to chlorine bleaching. Tear strength is moderately reduced.[22,23,24,25,26]

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[17] Refer to note 10, page 4-4.

[18] Hindersinn, Raymond R.; G.M. Wagner. Fire retardancy. In Encyclopedia of Polymer Science and Technology, John Wiley & Sons, N.Y., 1967 (OTS-AA-0338)

[19] Daigle, D.J.; et al. Modifying THP (tris (hydroxymethyl) phosphine)-amid=flame retardant. American Dyestuff Reporter, 62 (6): 57-9, 80, (1973) (OTS-AA-0020)

[20] Linden, P.; S.B. Sello, H.S. Skovronek. Flame resistance of polyester/cellulosic blends. Texilveredlung, 6 (10): 651-6, (1971) (OTS-AA-0067)

[21] Daigle, Donald J.; D.J. Donaldson. Less expensive durable flame retardant. Textile Chemist & Colorist, 1 (24): 534-6, (1969) (OTS-AA-0271)

Mazzeno has studied the major phosphorus-based system for the effect of u.v. radiation. All the present systems were found to decompose to water-soluble products including formaldehyde and hydrogen chloride. The products of degeneration were subject to leaching. Tris(1-aziridinyl) phosphine oxide was found most resistant. Heat, moisture and u.v. radiation resulted in decomposition of the finishes.[27]

Effects of laundry variables have been investigated by Perkins, Drake and Reeves.[28,29] Although modifications in the application procedures have significant effect on the resistance of the durable flame retardant finishes to ion exchange and leachability, the effectiveness of all cotton

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[22] Beninate, John V.; et al. Conventional pad-dry-cure process for durable-flame and wrinkle resistance with tetrakis (hydroxymethyl) phosphonium hydroxide (THPOH). Textile Research Journal, 38 (3): 267-72, (1968) (OTS-AA-0007)

[23] Refer to note 11 on page 4-5.

[24] Refer to note 12 on page 4-5.

[25] Beninate, John V. Better flame resistant finish for cottons. Textile Industries, 131 (11): 110,112,114,116,118, (1967) (OTS-AA-0128)

[26] Daigle, D.J., op. cit.

[27] Mazzeno, L.W.; et al. Degradation of selected flame retardants on exposure to u.v. and elevated temperatures. Text. Chem. Color, 5 (3): 55-9, (1973)(OTS-AA-0077)

[28] Perkins, R.M.; G.L. Drake, Jr., W.A. Reeves. Effect of laundering variables on the flame retardancy of cotton fabrics. Colourage, 18 (24): 33-6, (1971) (OTS-AA-0222)

[29] Perkins, R.M.; G.L. Drake, Jr., W.A. Reeves. Effect of laundering variables on the flame retardancy of cotton fabrics. Journal of American Oil Chemists Society, 48 (7): 330-3, (1971) (OTS-AA-0223)

treatments is reduced by laundry detergents. As with the semidurable cellulose phosphate esters, the loss of efficacy is most likely a result of ion exchange rather than leaching of the phosphate-containing components. Nonphosphate detergents are significantly more deleterious than phosphate detergents, although phosphate retention in the treated fabric remains fairly constant through successive washings with either type detergent. Soap and softwater washings have little or no effect on the efficacy of the flame retardants, thus bolstering the theory that ion exchange is responsible for loss of flame retardance in the wash. In a later study, Le Blanc reported similar results for the THPC-based systems, but Pyrovatex, the phosphonoalkanoicamide-based treatment, showed superior resistance to ion exchange from calcium antagonism.[30]

The physical properties of THPC-finished cotton vary considerably depending on the applications. It is possible to produce finished products with an acceptable hand and drape. This is usually accomplished with some loss of effectiveness. The newer methods have wash and wear characteristics. Fabric stiffness and reduction in tearing strength are still a problem.

## 4.3 ECONOMIC CONSIDERATIONS

Economic considerations are a factor of:

- Producers
- Markets and uses
- Transportation

### 4.3.1 Producers

Table 4-1 lists the commercial durable and semidurable flame retardants and their manufacturers.

Specific production figures for the different treatments were not identified. There are clear implications that Ciba-Geigy's Pyrovatex, the ammonia-THPC finish, and the THPC-trimethylolmelamine (TMM) finishes now dominate

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[30] LeBlanc, R. Bruce; D.A. LeBlanc. Effects of calcium deposits on fire retardant cotton. Amer. Dyest. Rep., 62 (3): 50, (1973) (OTS-AA-0063).

TABLE 4-1. SUPPLIERS OF SEMIDURABLE AND DURABLE FLAME RETARDANT TREATMENTS[1]

| Company and Trade Names | Active Chemicals | Form | Durability | Treated Fibers |
|---|---|---|---|---|
| Amalgamated Chemical<br>Fireseal | Organic Phosphorus | Liquid | Semidurable | Cellulosics |
| American Cyanamid<br>Pyroset | Phosphorus, Nitrogen | Water solution | Semidurable & | Silk, Cellulosics, Wool |
| Apex Chemical<br>Flameproof | Not available | Liquid, Powder | Semidurable & durable | Varied |
| Ciba-Geigy<br>Pyrovatex | N-methylol dimethyl phosphonopropionamide | Water solution | Durable | Cellulosics |
| Dooley Chemical<br>D-C Tex 211P | inorganic chemical complex | Liquid | Semidurable | Varied |
| D-C Tex 220 | Not available | Liquid | Semidurable | Varied |
| Dover Chemical<br>Chlorez | Chlorinated Paraffins | Powder | Semidurable | Latexes |
| Rez-O-Sperse | Chlorinated Paraffins | Water solution<br>Emulsion | and | Latexes |
| Paroil | Chlorinated Paraffins | Liquid | Durable | Latexes |
| Dow Chemical<br>(Tris-(1-Aziridinyl) phosphine oxide<br>(may be discontinued) | APO | Liquid | Durable | Cellulosics |
| Fancourt<br>Fire Retardant | Boro-Phosphate | Powder | Durable | Cellulosics |
| Hooker Chemical<br>THPC | Tetrakis (hydroxymethyl) phosphonium chloride | Water solution | Durable | Cotton, Wool |
| Inmont<br>Fire Retardant 9153 | Antimony oxide | Liquid | Semidurable | Varied |

TABLE 4-1. (Contd.)

| Company and Trade Names | Active Chemicals | Form | Durability | Treated Fibers |
|---|---|---|---|---|
| Monsanto<br>MCC/100 | Proprietary phosphorus | Water solution | Durable | Cellulosics |
| Moretex Chemical<br>Moretex TOP Emulsion | Phosphate ester | Emulsion | Not available | Varied |
| National Lead<br>Oncor | Antimony Oxide | Powder | Not available | Varied |
| Neville Chemical<br>Unichlor | Chlorinated Paraffins | Liquid & Powder | Semidurables | Varied |
| Dr. Quehl<br>Aflamman | Phosphorus-Nitrogen | Dispersions, Water & Oil Solutions | Semidurable | Cellulosics & non-cellulosics |
| Aflammit | Organic Phosphorus-Nitrogen | Water Solution | Durable | Cellulosics & Blends |
| Proban | THPC | Water Solution | Durable | Cellulosics, Wool |
| Sanitized Chemical<br>Saniflamed | Organic Phosphorus, Nitrogen | Liquid | Durable | Cellulosics |
| Swift & Co.<br>Brominex | Bromine, Nitrogen & Phosphorus | Liquid | Semidurable | Cellulosics |
| Syntheron<br>Fyre-Fix | Not available | Water Solution | Durable | Cellulosics |
| White Chemical<br>Series C | Bromine, Phosphorus & Bromine Phosphorus organics | Not Available | Durable | Cellulosics |

[1] Source: American Dyestuff Reporter, January 1972.

the flame retardant finishing of cotton fabrics. Several chemical companies may market THPC-based systems under proprietary manufacturing patents, but Hooker Chemical Co. is the leading manufacturer of the compound. Textile finishing companies are responsible for production of the actual flame retardant fabrics and employ the systems described previously to produce the final product.

When THPOH is used alone, the chemical cost to consumers, prior to the current inflationary period (1972), was about 12¢ per square yard of treated fabric. Combination treatments with trimethylolmelamine in a ratio of 2:1, THPOH:TMM dropped the cost to about 8.7¢ per square yard. The incorporation of additional amounts of TMM does not reduce the cost any further.

The dominant position of the THPC/OH system as a flame retardant treatment for cotton fabric is favored by ordinary economic considerations. Although it is likely that technically improved compounds and systems will be produced by the synthesis of related methylol phosphine oxides, it is not likely that the cost effectiveness ratio will be superior to the THPC/OH systems. The advantage is in the relative low cost of the starting materials: phosphine, formaldehyde and hydrogen chloride.[31,32,33] American Cyanamid is reportedly planning a major capital investment in a Canadian plant to produce phosphine less expensively than it is currently produced. Since phosphine is the most costly starting compound, this development could eventually lead to a lower cost of THPC/OH-based systems.

### 4.3.2 Principal Markets and Uses

Until recently, textile uses for chloroparaffin-antimony oxide systems have been almost exclusively for outdoor canvas and cotton duck treatment for military products such as tents and tarpaulin. The growth market currently

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[31] Chance, Leon H.; J.P. Moreau, G.L. Drake, Jr. Flame retardant for cotton based on THPOH (tetrakis(hydroxymethyl) phosphonium hydroxide) and guanazole. Journal of Coated Fibrous Materials, 2 (3): 161-72, (1973) (OTS-AA-0017).

[32] Chance, Leon H.; W.E. Reeves, G.L. Drake, Jr. Phosphorus-containing carboxamides and their evaluation on cotton fabrics. Textile Research Journal, 35 (4): 291-8, (1965) (OTS-AA-0137).

[33] Chance, Leon H.; E.K. Leonard, G.L. Drake, Jr. Methylol derivatives of halocyanoacetamides and their evaluation on cotton fabrics. Textile Research Journal, 37 (5): 339-43, (1967) (OTS-AA-0153).

being experienced is related to the use of these systems in conjunction with thermoplastic polymers such as polyvinyl chloride, rather than for textile use. The construction industry and the automotive industry are now using these as additives to produce a variety of flame retardant polymer products, especially electrical coatings.

There is a civilian consumer market for flame retardant finishes durable through five to ten launderings and dry cleaning. Cost is an important factor and should add no more than 10-15 cents per yard of finished goods. Any higher cost puts fabrics so treated into competition with durable treatments where the advantages of superior performance, particularly with regard to flammability testing standards, outweigh modest cost differentials. The semidurable treatments have no clearly defined consumer market of their own. They compete with both nondurable treatments and durable treatments for fabrics used as curtains, drapery, mattress ticking, blankets, and plush toys.[34] The original standards for testing of mattresses included a leaching procedure that might have adversely affected the semidurables in that market, but revised standards (DOC FF-4-72) have been more lenient. However, no data were retrieved to show specifically that the semidurable treatments have benefited from the growth market for flame retardant bedding.[35]

In general, the market for durable flame retardant fabrics produced by chemical aftertreatment and finishing has benefited very little from the growing interest in flame retardant products. The THPC/OH systems and Pyrovatex have accounted for virtually all the permanent fire retardant systems for cotton since they have been introduced commercially. Outside of the markets created by flammable fabric legislation, there has been limited consumer demand for flame retardant cotton. Until 1968, the military and some institutional uses were the principal markets. In 1971, when the civilian uses began to be significant, it was possible to produce flame retardant cottons for an additional 13-15 cents per square yard in full production. In practice, the still limited market made flame retardant fabrics a specialty business that actually cost about 25 cents per square yard or higher. By 1973, non-flame retardant cotton flannel cost 45 cents a square yard and flame retardant cotton flannel cost 72 cents a square yard. By the end of 1974 flame retardant cotton flannel ranged from 90 cents to $1.05 a yard.

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[34] LeBlanc, R. Bruce. Flammability and fire resistance of textiles. American Dyestuff Reporter, 57 (27): P1093-P1096, (1968) (OTS-AA-0348).

[35] Refer to note 14, Section III, page 3-11.

In addition to these direct cost considerations, testing of end products using cotton adds to the processing time and complicates inventory control systems. While the tests are in progress, the product continues to roll off the finishing line at a rate of 50 to 100 yards per minute. Test failures or inconclusive results require a decision to reprocess the goods or to hold them in inventory and delay shipping to customers pending the outcome of the testing. These problems put cotton at a significant disadvantage in competition with man-made fibers that are inherently more flame retardant than cotton and have a better chance of consistently passing the product flammability tests.

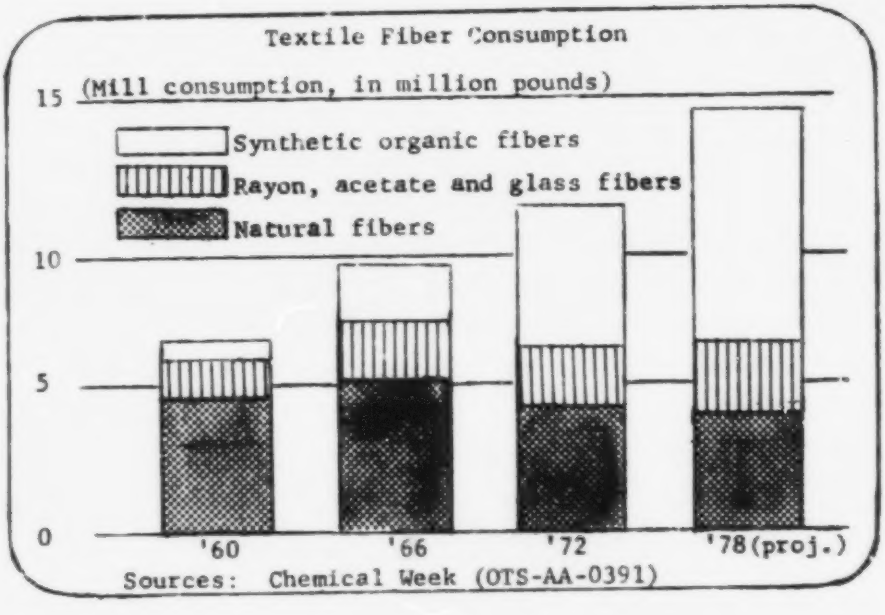
The drastic effect that the flammable fabrics testing program has had upon the flame retardant textile market is demonstrated both in the American and the British markets. In Britain, the pretesting period gave Proban cotton, a THPC-treated fabric, the dominant position for children's sleepwear. With the advent of testing, there is practically no cotton being consumed by this market. In the United States, cotton in 1971supplied 78 per cent, or 27 million pounds of the material used to produce size 0-6X sleepwear. In 1973, treated cotton provided less than 10 percent, or only 3 1/2 million pounds.

The initial effectiveness of the THPC/OH systems and Pyrovatex have never been in question for use on cellulose. In markets where cotton is able to compete, THPC/OH systems and phosphonoalkanoicamides will hold their respective positions as the treatments of choice. Government contracts for military textile products and Veteran's Administration Hospitals will continue to provide the largest market. Non-military hospitals have also been a fair sized market for durably treated cubicle curtains. Steel mills were previously a significant market for flame retardant work clothes, but automated processing has reduced the number of people who work around open flames and blast furnaces.

Three factors have combined to prevent the increased use of the durable flame retardant treatments for cellulosic fabrics:

1. Cotton has lost much of its market position to man-made fibers. Polyesters, acetate and triacetate fibers have gained market position at the expense of cotton.
2. Flame retardant cotton has been unable to consistently pass the stringent test for durability used to measure flame retardance of apparel, carpets and sheeting.
3. The durable cellulosic treatments have only limited effectiveness for use with cotton/man-made blends.

The diminished role of cotton, rayon and wool in the worldwide textile market is a result of short supply, rising costs and stiff competition from the man-made fibers. The U.S. Department of Agriculture predicts this trend to continue through 1979, at least. Cotton markets that will suffer include apparel, home furnishings, automotive and industrial markets. Polyester fibers will be the leading gainer. The changing market picture from 1960 projected through 1978 is shown in Figure 4-1.



Sources: Chemical Week (OTS-AA-0391)

Figure 4-1

The cost and processing difficulties brought about by durable flame retardant treatments notwithstanding, cotton's use in textiles is declining. The reasons for this decline have not been investigated within this study and there may not be a direct correlation between the declining cotton market and the decline of cotton in the flame retardant textile market. However, an apparent correlation does seem to exist, at least for the civilian consumer market.

Factors that could favor cotton are increased cotton crops, which are not expected for this year, and a shortage of feedstock chemicals for the man-made fibers. Ethylene glycol shortages have already caused production cutbacks of polyester supplies. Restricted production of polyvinyl chloride due to toxicity will reduce the supply of modacrylics. Shortages of dimethylterephthalate, terephthalic acid, caprolactam and cyclohexane are also predicted and will further reduce the supply of the man-made fibers.[36] The real influences specifically affecting the flame retardant textile markets cannot be predicted with any accuracy. These influences are mentioned because of their potential to drastically change the current and predicted textile market picture and indirectly affect the textile flame retardant market.

The THPC/OH systems and Pyrovatex have both been unable to consistently pass the 50 laundering requirements for durability. While it has been shown experimentally that careful formulation, application and product design can produce the durability required of the tests, until it can be done commercially in a full plant operation, treated cotton will be at a serious disadvantage compared to modified man-made fibers.[37]

The loss of flame retardant effectiveness in laundering short of 50 washes has also prevented the use of cotton in blended fabrics with the man-made fibers. Untreated cotton, when present in blends, tends to act as a wick in combustion. Blended fabrics that would otherwise snuff out a flame continue to burn with the cotton acting as a wick to hold the flame and the thermoplastic fibers feeding the flame. The blends are more hazardous than a fabric of either fiber alone. Tesoro and associates have described this phenomenon and demonstrated the need to apply topical finishes to fabrics made from blends of a non-flammable fiber with a flammable one, whether it is cellulose or some other.[38,39,40] Le Blanc further tested a variety of cotton/polyester treated blends and came to the conclusion that THPC systems are superior to Pyrovatex for use on cotton/polyester blends. But, THPC gives a finish having adequate fire retardance and adequate hand only when the polyester content is 25 percent or less. Pyrovatex gives a superior hand but is said to be ineffective with blends of more than 12.5 percent polyester.[41]

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[36] Anonymous. Worldwide boom in textile goods spins prosperity for fiber firms. Chemical Week, 113, (2): 18-19, (1973) (OTS-AA-0391).

[37] Refer to note 19, page 4-7.

### 4.3.3 Transportation

No clear inferences on transportation patterns or practices relating to textile flame retardants were taken from the data retrieved in this study.

## 4.4 ENVIRONMENTAL IMPLICATIONS

Environmental implications of semidurable and durable flame retardant textile treatments relate to their manufacture and use. The meaning is interpreted broadly to include air, water, and soil pollution, as well as toxicity to humans and other living organisms. Enviornmental contamination, monitoring and analysis techniques, reactivity, biology, environmental effects, and toxicity are specific items incorporated into this section. The flame retardants themselves, and the by-products of their manufacture and use are the compounds of interest.

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[38] Tesoro, Giuliana; S.B. Sello, J.J. Willard. Flame-retardant properties of phosphonate derivatives of cotton cellulose. Textile Research Journal, 38 (3): 245-55, (1968) (OTS-AA-0196)

[39] Tesoro, Giuliana C.; C.H. Meiser. Effects of chemical composition on the flammability behavior of textiles. Textile Research Journal, 40 (5): 430-6, (1970) (OTS-AA-0197)

[40] Tesoro, Giuliana C.; J. Rivlin. Flammability behavior of experimental blends. Textile Chemist & Colorist, 3 (7): 156-60, (1971) (OTS-AA-0198)

[41] Le Blanc, R. Bruce; E.R. Gray. Fire retardant finishing of polyester/cotton blends. Textile Chemist & Colorist, 3 (12): 263-5, (1971) (OTS-AA-0062)

### 4.4.1 Contamination

The textile industry is a significant source of localized environmental contamination. Pressure is being exerted to reduce or control the industry's waste production. The literature indicates a willingness on the part of the industry to comply with regulations and public demands, but the mills are scattered and the diversity of materials used in textile processing make total compliance a complex and costly procedure. Resins, including flame retardant treatments, are only a minor part of the overall problems created by the textile mills. A general review of the contamination contribution from textile wastes is provided by Burr.[42] Major types of textile mills and their wastes are listed. Biochemical oxygen demands (BOD) of principal chemical wastes are listed, but textile resins are not seen as a serious problem.

Contamination control in the textile industry requires a balanced state considering water pollution, air pollution, solid waste disposal, and occupational safety and health problems. Water pollution is the most serious problem because water treatments have been used extensively in the industry for applying textile finishes. Moves to employ organic solvent systems are resisted because of the capital investment required, and the technology seems to exist that would enable manufacturers to easily reduce their water usage and meet with the federal guidelines set at 5000 to 35,000 gallons of water per 1000 lbs. of cloth or fiber.[43] Improvement of the water usage problem can create problems in other ways.[44] More concentrated effluent will raise the BOD and the solid contents will be higher. Use of organic solvents creates problems of worker exposure to toxic fumes. Concentrated ammonia fumes, hydrogen chloride and formaldehyde are the most serious volatiles associated with flame retardant materials. Where gaseous vapors are not recovered in solution, concentrated vapor fumes are often ventilated into the atmosphere.[45]

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[42] Refer to note 15, Section III, page 3-13.

[43] Refer to note 17, Section III, page 3-14.

[44] Alspaugit, T.A. Textile wastes. J. Water Pollution Control Fed., 43 (6): 1001-1008, (1971) (OTS-AA-0381).

[45] Refer to note 18, Section III, page 3-14.

In textile mill water effluent discharges, the finishing chemicals are usually biodegradable, but they are also highly reactive and form derivatives in reaction with other chemicals present in the water systems. The colloidal resins themselves are not biodegradable. Whether these initial products are toxic or harmful is not known.[46] The components of the resin systems are known to continue to resinify in sewage lines and occlude other undesirable ingredients such as dyes and unreacted molecules of the finishing processes.[47]

Heat and moisture have been shown to degrade the permanent finishes of treated fabrics. Some of the THPC/OH finishes have been shown experimentally to give off detectable formaldehyde, hydrogen chloride and phosphine for up to two months after finishing.[48,49]

Several methods for qualitative or quantitative analysis of durable flame retardant-treated textiles were retrieved. One method potentially useful for monitoring water pollution related to textile finishes was also retrieved. Analytical methods for determining flame retardant finishes were described for cool flame emission spectroscopy,[50] gasometric determination of THPC[51] and infrared spectroscopy.[52] The cool flame spectroscopic technique of Elliot is inappropriate for durable finishes, since residual acids as nitrates and sulfates gave high background emission readings that interfere with the results. Ellzey and Connick have developed a gasometric analysis technique for assaying THPC in commercial solutions. It involves the collection and measurement of the volume of hydrogen evolved from the reaction of THPC and NaOH. It is inexpensive, rapid and precise for the intended use. Results were compared with NMR techniques, titrations, infrared spectroscopy and precipitation. The reported method was shown to be as accurate as any other. Morris and associates have described a method for extracting THPC from fabric finishes in such a way as to facilitate infrared identification of the compound.[53] They were concerned that there is no special catalog of infrared spectra for the components of fabric finishes. In an effort to start such a catalog, they publish their spectrographs for the most popular THPC/OH finishes.

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[46] Porter, John J.; D.W. Lyons, W.F. Nolan. Water uses and wastes in the textile industry. Environmental Science and Technology, 6 (1): 36-41, (1972) (OTS-AA-0361).

[47] Refer to note 16, Section III, page 3-14.

[48] Afanas'eva, L.V.; N.S. Evseenko. Hygienic evaluation of fireproof textiles processed with an organophosphorus impregnant based on tetrahydroxymethyl phosphonium chloride. Hygiene and Sanitation, 36 (3): 450-453 (1971) (OTS-AA-0363).

[49] Refer to note 27, page 4-8.

[50] Refer to note 20, Section III, page 3-15.

[51] Ellzey, S.W., Jr., W.J. Connick, Jr. Gasometric determination of THPC (tetrakis (hydroxymethyl) phosphonium chloride). Amer. Dyestuff Reporter, 62 (6):, 47, 50, (1973) (OTS-AA-0036).

[52] Nelson, K.H.; W.D. Brown, S.J. Staruch. Rapid determination of bromine-containing flame retardants on fabrics. Textile Research Journal, 43(6): 357-61, (1973) (OTS-AA-0083).

A very recent procedure has been published by Lysyj for a qualitative analysis of mixed organic industrial composition wastes by pyrographic techniques. Textile mill wastes are discussed by way of example. An automated monitoring procedure is claimed to have resulted from Lysyj's work that is sensitive to single organic compounds that manifest themselves on a pyrogram as peaks with identical retention times by varying intensities. The variations produce common patterns specific to parent materials.[54] Production-type instruments have been produced and fabricated. Practical implementation of pyrography for stream surveillance has been achieved in two sites. The author claims that overall patterns of river water can be interpreted in terms of specific contributing waste patterns.

Although inferences of potential contamination resulting from the use of durable flame retardants for textiles have been made in this section, the only clearly dangerous textile flame retardant per se is tris(1-aziridinyl) phosphine oxide (APO). The chemical reactivity of APO would facilitate its hydrolysis in waste effluence and it is unlikely that the unreacted monomer would reach even the treatment plant. As noted previously, APO may not be available at this time. But the nature of textile mill effluent is not known and there is little indication in the literature that the industry has considered the contamination problem posed by a known toxicant that had been widely used in combination with THPC until very recently. The need to characterize industrial waste in general, and the textile finishing wastes in particular, is quite clear.

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[53] Morris, Nancy M.; E.R. McCall, V.W. Tripp. Identifying finishes by infrared spectroscopy. Fluorochemicals and flame retardants. Textile Chemist & Colorist, 4 (12); 283-6, (1972).

[54] Lysyj, Thor. Pyrographic analysis of waste waters. Environmental Science and Technology, 8 (1): 31-34, (1974) (OTS-AA-0384).

### 4.4.2 Biology and Toxicity

The toxicology profile of the durable flame retardants for textiles is likely to be unique for each of the systems. The crosslinking agents, the amount of add-on, the different cures, the substrate material, and even the processing conditions affect the durability, the presence of residue in the fabric and the products of decomposition. What is true for one treatment is not necessarily true for all. Thus, each variation would have to be studied independently in order to fully characterize the toxicology of the class. No studies were identified which approach such a broad-based comparison. Specific studies did document the particular treatments investigated.

The THPC-ammonia systems might be expected to have a somewhat different toxicology than the THPC-TMM systems by virtue of the relative difference in the amount of formaldehyde groups present in the two product polymers. The THPOH ammonia cure process reduces the presence of HCl in the manufacturing processes and may result in a lower level of chloride residue on finished fabrics.

For THPC/OH systems, the most serious problems seem to be related to formaldehyde and hydrogen chloride. The spontaneous formation of these compounds or their presence as a residue is a source of toxicity. Notably, in general use there has been an extremely low incidence of reactions to THPC/OH based flame retardant materials. In one study, less than one percent in a study group of over 200 men and women exhibited any reaction and formaldehyde was assumed to be the toxicant.[55] Wilson, in a comparative study of APO solution, THPC solution and respectively treated cloths, found no evidence of significant THPC toxicity when topically applied to guinea pigs and rabbits, although slight leukopenia was observed. However, other investigators have noted that the popular THPC/OH systems decompose in a warm, moist environment and yield formaldehyde and hydrogen chloride. Mazzeno has shown this is true in vitro for the finishes now used in the American market.[56] Afanas'eva, in a Russian study, showed that six THPC formulations, including Proban, would liberate formaldehyde into the air, and formaldehyde, hydrogen chloride, and organophosphorus compounds into an aqueous medium continuously for one to two months. Both local irritant and systemic effects were noted. Blood counts showed leukopenia and the organophosphorus compounds inhibited cholinesterase activity 20 to 40%. Topical applications of aqueous extracts resulted in death of 50-70% of the experimental mice. However, the dosage was not reported. Afanas'eva concluded that THPC-treated materials were inappropriate for work clothes worn in a warm, and humid environment.[57] If these facts are borne out, THPC-treated fabrics may also be hazardous when used for sleepwear and blankets for children at an age when they tend to suck the products, or might wet their bedclothes.

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[55] Martin-Scott, Ian. Contact textile dermatitis (with special reference to fireproof fabrics). British Journal of Dermatology, 78 (12): 632-635, (1966) (OTS-AA-0365).

The decomposition of THPC/OH into formaldehyde and hydrogen chloride raises another serious question. Investigators have shown that bis-chloromethyl ether (bis-CME), a carcinogen, can form spontaneously in ordinary humid air. Although there is some disagreement about its carcinogenicity in humans, bis-CME has caused lung cancer in rats and the evidence strongly suggests it has produced cancer in chemical workers. The current controversy centers on whether sufficient concentrations of formaldehyde and hydrogen chloride are present in work environments to form bis-CME that can threaten workers. Investigations specific to THPC textile flame retardants apparently have not been made.

Abnormally high concentrations of formaldehyde and hydrogen chloride in a humid atmosphere could exist in textile waste effluents, THPC in treated clothing that is wet and warm, or in the superheated environment of a building fire. It is conceivable that THPC could generate sufficient formaldehyde and hydrogen chloride to spontaneously produce traces of bis-CME under such special conditions.[58]

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[56] Refer to note 27, page 4-8.

[57] Refer to note 48, page 4-18.

[58] Kallos, G.J.; R.A. Solomon. Investigations of the formation of bis-chlormethyl ether in simulated hydrogen chloride-formaldehyde atmospheric environments. American Industrial Hygiene Assoc. Journal, 34 (11): 469-473, (1973) (OTS-AA-0376).

A limited incidence of contact dermatitis attributed to formaldehyde has also been associated with flame retardant clothing.[59,60]

Pyrovatex, by comparison, is claimed to be less toxic than the THPC systems and APO. Only the original papers describing the Ciba-Geigy phosphonoproprionamide compounds make mention of its toxicity and they provide no data to support the claim.[61,62] Pyrovatex has been shown to decompose to water soluble products in a manner similar to THPC.[63] Tris (1-azirdinyl) phosphine, although it is no longer used as extensively as once was thought, is the most toxic chemical used in durable flame retardant treatments for cellulosic textiles. The unreacted monomer was shown by Wilson to be lethal when topically applied in solution to mice and rabbits. APO treated fabrics, on the other hand, were not toxic.[64] Mazzeno, in his study of the resistance of treated fabrics to u.v. radiation, concluded the APO performed better than other treatments and did not degrade to the toxic monomer. The performance of APO in combustion was not investigated, so that the question of whether or not APO monomer could be generated in a fire is open.[65] Sram investigated APO as a genetic mutagen.[66] He demonstrated a direct correlation between dose of APO and the frequency of dominant lethal alleles manifested in male mice. Doses of 1 mg. of APO per kg. of body weight were sufficient to induce mutagenicity.

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[59] Jordan, William P. Clothing and shoe dermatitis. Recognition and management. Postgraduate Medicine, 52 (5): 143-148, (1972) (OTS-AA-0364).

[60] Refer to note 58, page 4-22.

[61] Refer to note 9, page 4-4.

[62] Refer to note 10, page 4-4.

[63] Refer to note 27, page 4-8.

[64] Wilson, Robert H. A note on skin tests of flame retardant materials. Textile Research Journal, 32 (5): 424-425, (1962) (OTS-AA-0371).

[65] Mazzeno, L.W.; et al. Degradation of selected flame retardants on exposure to uv and elevated temperatures. Text. Chem. Color, 5 (3): 55-9, (1973) (OTS-AA-0077).

[66] Sram, R.J.; Z. Zudova. Effect of the dose-fractionation on the frequency of Chromosome abberations induced in mice by TEPA. Folia Biologica, 19 (1): 58-67, (1973) (OTS-AA-0357).

## 4.5 SUMMARY AND CONCLUSIONS

For treatment of cotton, rayon and to some extent the other natural fibers, THPC and Pyrovatex are adequate to flame retard textile products. However, some growth markets are closed to them until treatments are perfected for commercial use that will consistently pass the leach requirements of 50 home launderings. Cotton's general loss of market position is the most significant factor likely to keep the use of durable cellulosic flame retardant treatments a limited specialty market catering mostly to the military contracts and institutional drapery and bedding. In the current market, any additional finishing costs are detrimental to the sale of cotton products. The inefficient flame retardance of cellulosic treatments on blended fabrics is particularly limiting, as it ties their use to products made of 75 percent or more cotton.

The nature of flame retardant cotton finishings is unlikely to take any drastic changes from the treatments described here. A clearer picture of the civilian market for treated cotton might be developed by more intensive study; and the relative uses of the many variant systems might be investigated further. The chemistry of the technology as it affects the products and by-products of the variant treatments is also worth further study.

As a known hazard, these flame retardant systems present only a minor occurence of dermatitis. By-products of the manufacture and products of degeneration are more serious problems. In relation to the overall problems associated with disposal of textile mill wastes, the by-products of manufacture are unlikely to be significant. The special conditions under which THPC/OH systems might result in the generation of bis(chloromethyl) ether or other obnoxious products are of particular interest with regard to the durable flame retardant. It is not likely that such investigations have been reported previously, or they would have been revealed in the literature. An original investigation of the problem should be undertaken under the sponsorship of an appropriate Federal agency. Additional work to test the validity of Afanas'eva is also indicated, as a search of Science Citation Index indicated there has been no follow-up study to date.

## SECTION V. MAN-MADE TEXTILES

The current era of textile flame retardance is characterized by flammability standards that define the effectiveness and permissable uses of flame retardant chemicals according to their durability and performance in standardized test procedures. Products rather than textiles are the subject of testing. The standards not only affect the natural and man-made fibers used in the tested products, but also the design and construction of the products. The fibers used in carpets, rugs and bedding, are generically the same as those used in children's sleepwear and other apparel. But chemical modifications and treatments that impart flame retardance to acrylic fibers used for carpeting may be unacceptable or inadequate as flame retardants for children's sleepwear. Either test failure or failure to meet aesthetic, comfort, and ease of care requirements demanded by consumers is sufficient to limit the usefulness of a technically effective flame retardant. Manufacturers have a choice whether to make flammable fibers flame retardant, or to use materials in product construction that are inherently less flammable than traditional fibers. In the choice of textile fibers, should a manufacturer choose to use cotton fabrics, an aftertreatment such as those described in Sections III and IV are adequate to the task given appropriate end uses and compliance with Federal standards. If the choice is to use man made fibers, the fibers themselves can be tailored to meet the specific requirements of appropriate standards through chemical modification with appropriate comonomers or addition of additives and coreactants in their manufacture; or they can be aftertreated like the cotton materials. Initially, manufacturers chose to use inherently less flammable textile fibers as a starting material, particularly where compliance with flame retardant standards was required. When shortages of inherently flame retardant fibers (e.g., modacrylics) occurred, new techniques for aftertreatment of polyesters and polyolefin were developed which proved to be superior to treatments of cotton.

With the demand for flame retardant textile products increasing as a direct result of legislation, man-made fiber producers and the chemical industry turned to the technology of flame retardance for plastics and used it to create thermoplastics and resins for textile uses in products designed to meet the standards through a combination of less flammable materials and product design. This is borne out by the character of the flame retardant textile literature since 1972. At that time, there was a paucity of journal articles on effective flame retardant man-made fibers. Modacrylics, vinyl fibers and specialty high temperature nylon were available and were considered to be inherently flame retardant textiles. No truly effective treatments were claimed for the popular polyesters, polyolefins, polyamides or blends of these fibers alone and with cotton. In the literature retrieved since 1972, over 600 patents (65% of the literature base) were noted that claimed flame retardant modifications to produce inherently less flammable polymeric materials. Modified and treated polyesters are particularly well represented. However, a comparison of the patent claims with general articles on plastic technology showed that the trend is to add flame retardant properties to man-made fibers with the use of resins, plasticizers, and stabilizers developed for plastic products that incidentally have been shown to impart some degree of flame retardance or melt inhibition to the resulting polymer.

The great variations possible in synthetic polymer chemistry, and the control of the physical properties that can be exercised by additives and precise tailoring of the comonomers make the ultimate situation with regard to flame retardant, man-made textile fibers less clear than with cotton and other natural fibers. Lyons has provided a general review of flame retardance of polymers.[1] In the process, he has related the technology to the production of man-made fibers from polyolefins, vinyls, acrylics, polyesters, and polyamides. However, what remains particularly unclear with regard to the man-made fibers is whether the breakthroughs in the technology of flame retardance will come by incorporating comonomers containing flame retardant elements (phosphorus, nitrogen, volatile metals, chlorine and bromine) into today's textile polymers, or from improved aftertreatment; or, entirely new, textile polymer structures will be synthesized which are inherently flame retardant or even fire proof.

The chemical industry alone is reportedly spending between 10 and 20 million dollars annually on flame retardancy research. With the intensity of current research, it is likely that a number of important, new chemical principles will be commercially developed in the next few years that are not significant as of this writing. However, the flame retardants investigated in the course of the intensive phase of this study represent virtually all of what is being used to achieve durable flame retardancy in textile materials at this time.

## 5.1 STRUCTURES AND PROPERTIES

The chemicals with which the project was concerned in the intensive phase of the investigation consisted of four chemical types used in the manufacturer of man-made fibers and textiles derived therefrom.

The broad scope the subject area required that the materials be considered in an order of priority:

1. Halogenated polymers of textile polyesters, polyamides, and modacrylics. Homopolymers, copolymers, and oligomers solely of haloolefins (e.g., vinyl chloride, vinylidene chloride and vinyl alcohol) and all elastomers were specifically de-emphasized.

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[1] Lyons, John W. The chemistry and uses of fire retardants, New York, Wiley-Interscience, 1970 (OTS-AA-0075)

2. Fibers containing coreactive and additive organophosphorus components and similar aftertreatments for man-made fibers.
3. Aramids - fibers in which the fiber-forming substance is a long chain, synthetic polyamide with the amide linkages on aromatic rings.
4. Other high temperature, synthetic, organic fibers.

Clearly relevant data that was retrieved for any of the four types has been incorporated into this report. Intensive investigation of the chemistry and toxicology of the halogenated polymers and phosphorus containing polymers was more extensive than the lower two priority types. Thus, the coverage of the higher priority types is most comprehensive.

### 5.1.1 Halogenated Polymers

Halogenated monomers that are used or have been reported as commercially viable flame retardants for man-made textiles are listed in Table 5-1. The list is comprehensive and overly representative of organohalogens that are used as coreactants in the manufacture of flame retardant fibers. It is important to note that the variety of chemical groups listed does not imply that organohalogen coreactants are currently the most important flame retardants. In fact, they are not very effective in aftertreatment processes, which account for a large share of the market.

Unless the flame retarded fiber is designed for a very specific market or product, it is more economical and marketable if the finisher treats only those fabrics which will go into the manufacture of regulated products. Less than 10% of all fibers used today require flame retardant properties.

### 5.1.2 Organophosphorus Coreactives, Additives and Finishes

Organophosphorus-based fiber modification in finishing account for the most successful techniques used for polyesters, acetates and blends, but not modacrylic fibers. Organic phosphorus compounds that are reported as commercial, semi-commercial and developmental products are shown in Table 5-2.

## TABLE 5-1. HALOGENATED MONOMERS FOR FLAME RETARDING TEXTILE POLYESTERS, POLYAMIDES AND MODACRYLICS

| | | |
|---|---|---|
| Diol Moiety Modification | - | Pentaerythritol Dichloride |
| | - | Chloropropanediols |
| | - | Mono-, Di - and Trichlorobutanediol |
| | - | Epoxylated Tetrachlorohydroquinone |
| | - | Halogenated Bisphenol A |
| | - | Glycidyl Ether of Pentahalophenol |
| Phthalic Anhydride Moiety Modification | - | Tetrachlorophthalic Anhydride |
| | - | Tetrabromophthalic Anhydride |
| | - | Chlorendic Anhydride |
| Vinyl Monomers | - | Vinyl Chloride |
| | - | Vinylidene Chloride |
| | - | Vinyl Bromide |

Tris (2,3-dibromopropyl) phosphate, by virtue of the fact that it is a successful additive for use with acetate and triacetate fibers, as well as the basis for a successful finish to polyester, nylon and acrylic fabrics is, by far, the most important flame retardant compound in use for man-made fibers, on a volume-used basis.

## TABLE 5-2. ORGANOPHOSPHORUS FLAME RETARDANT

Tris (2,3-Dibromopropyl) Phosphate

Bis (2,3-Dibromopropyl) Allyl Phosphate

Bis (2-Chloroethyl) Vinyl Phosphonate

Diethyl Vinyl Phosphate

Dialkylchloromethly Phosphonates

Diallyl-2-3-Dibromopropyl Phosphate

Diallylphenyl Phosphonate

Triaryl Phosphates

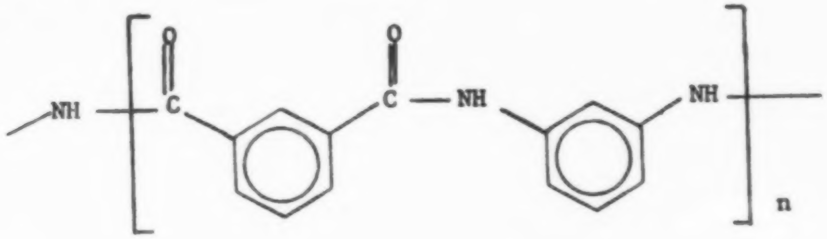
Polychlorophosphonates

Triallylphosphene Oxide

N-Methylol Dimethyl Phosphonopropionamide

### 5.1.3 Aramids

Aramids are a generic class of fibers having at least 85% aromatic-amide linkages. The first commercial aramid was marketed by E.I. duPont de Nemours & Company. The duPont product (Nomex)® is spun as a multifilament by a proprietary duPont process. The fiber is thermally stable above 300°C. The approximate structure is:



Monsanto has reported that they also have a semi-commercial aramid but the structure was not available.

The textile importance of the aramids is limited due to cost. Uses include hot air filtration fabrics, protective clothing for hazardous occupations, and special use materials for aircraft and boats.

### 5.1.4 Other High Temperature Synthetic Organic Fibers

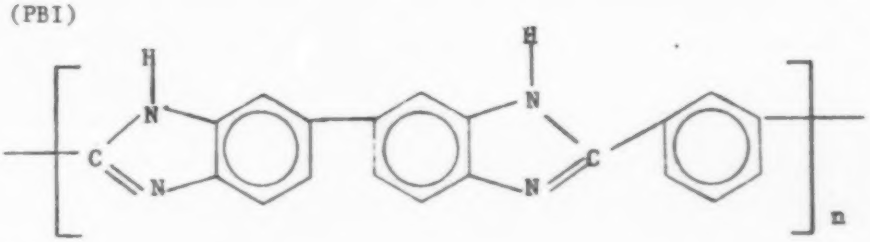
Aromatic components tend to impart thermal stability to polymers. Some heterocyclic rings have also been claimed to enhance flame retardance. Developments in the field of polymer chemistry, spurred mostly by the space exploration program, have resulted in fibers and polymers that conceivably could be used extensively in textile products by 1984. High production costs and limited supplies are the controlling factors for the moment that restrict their use to applications for which no substitute material is acceptable. As with the aramids, some have been used in race car driver gloves and overalls, firemen's clothing and space programs as well as high temperature industrial filters.

Kynol is a formaldehyde cross-linked aromatic fiber that is nearly fireproof. It is a product of the Carborundum Co. The structure was not available, but it is known to contain only carbon, hydrogen and oxygen. Kynol has had limited application for general consumer use because it has a brown color and it is brittle. A new version which is white is now in development. It can be dyed to any shade.

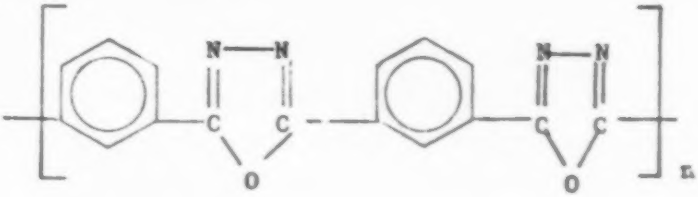
Other developmental high temperature fibers that appear to have significant potential for commercial development include polybenzimidazoles, polyoxadiazoles and a new duPont polyimide Kapton, which is a polypyromellitide more stable than Nomex. The generic structures for these synthetic polymers are shown in Table 5-3.

TABLE 5-3. HIGH TEMPERATURE SYNTHETIC ORGANIC FIBERS

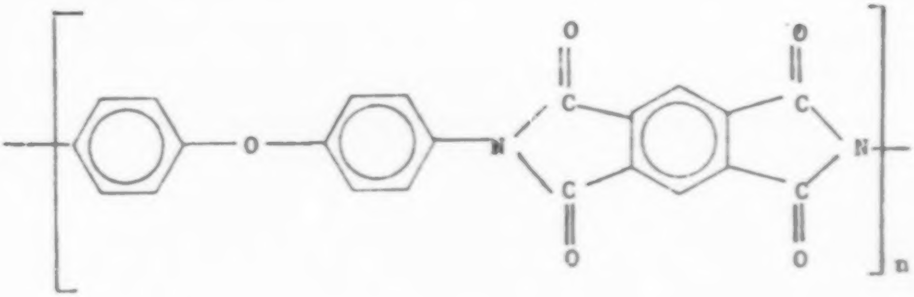
polybenzimidazole (PBI)



polyoxadiazole (PODZ)



polypyromellitide (Kapton)



### 5.1.5 Physical Properties

The choice of organohalogen and organophosphorus coreactants and additives is so varied that few generalizations can be made about the physical properties of man-made textiles made from these compounds. It has been claimed that except for the phenolic polymers, the flame retardant man-made textiles tend to yield more smoke, carbon monoxide and toxic fumes in laboratory-controlled combustion than natural materials.[2,3,4] The halogenated polymers yield hydrogen chloride or hydrogen bromide on heating.

Tris - 2,3 dibromopropyl phosphate as a commercial product is available in several grades. The major manufacturers - Michigan Chemical, Stauffer Chemical and Tenneco - report that the product used for flame retardant textile processes is a high grade compound that is 98% to 99% tris.[5] A list of tris properties is provided in Table 5-4.

Aromatic components of polymers add inherent thermal stability to thermoplastic polymers. Some heterocyclic compounds do the same. Phenolic resins, aromatic and heterocyclic polymers, aromatic epoxides and aromatic bromides are extremely unreactive and resist hydrolysis. As a result, this approach to flame retardance results in a relatively noncombustible char that forms at temperatures below the melting point of the fiber, but sufficiently high to resist combustion from ordinary sources of ignition.

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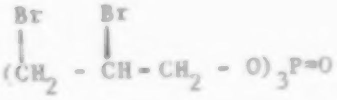
[2] Gaskill, James R., Smoke development in polymers during pyrolysis or combustion. Journal of Fire & Flammability, 1 (July): 183-216, 1970 (OTS-AA-0261)

[3] Carroll-Porczynski, C.Z., Application of simultaneous DTA TG and DTA/MS analysis for predicting in advance of processing the flammability and toxicity of gases of composite textile fabrics and polymers, In Thermal Analysis, Preceedings of the International Conference on Thermal Analysis 3rd, 1971, published 1972, 3, 273-84 (OTS-AA-0281)

[4] Carroll-Porczynski, C.Z., Fabric flammability. New testing methods and equipment. Textile Institute and Industry, 9 (7): 188-194, 1970 (OTS-AA-0300)

[5] Personal Communications

## TABLE 5-4. TRIS - (2,3 DIBROMOPROPYL) PHOSPHATE PROPERTIES[1]

| | |
|---|---|
| CHEMICAL NAME: | Tris-(2,3 dibromopropyl) phosphate |
| STRUCTURE: |  $(\overset{\overset{Br}{\vert}}{C}H_2 - \overset{\overset{Br}{\vert}}{C}H - CH_2 - O)_3P{=}O$ |
| GENERAL DESCRIPTION: | Tris is offered in two grades: standard and purified. The purified grade is offered for application in areas where improved heat stability, UV light stability, low volatiles and low color are of importance, e.g., polyurethane foams, expandable polystyrene beads and transparent or translucent polymers such as polyacrylates or polyesters. |
| MOLECULAR WEIGHT: | 697.7 |
| BROMINE CONTENT, %: | 68.7 |
| PHOSPHORUS CONTENT, %: | 4.4 |
| DENSITY @ 25°C: | g/ml 2.2 - 2.3<br>lbs/gal 18.4 - 18.6 |
| VISCOSITY, CS @ 25°C: | 4000 - 4200 (purified) |
| ACID NUMBER (mg KOH/g): | nil - 0.05 |
| COLOR (APHA): | 25-125 (purified) |
| VOLATILES: | 1.5 (purified) |
| SOLUBILITY: | Insoluble in water; miscible with $CCl_4$, $CHCl_3$, $CH_2Cl_2$ |

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[1] OTS-AA-0434 Tenneco Chemicals. Product Data Sheet, NUOGARD™ 23p
OTS-AA-0492 Stauffer Chemicals. Product Data Sheet, FYROL® HB-32

TABLE 5-4. (CONTINUED)

| | |
|---|---|
| HEAT STABILITY: | Although working temperatures as high as 390°C have been encountered in extrusion, calendering and milling, prolonged temperatures above 325°C are not recommended. |
| LIGHT STABILITY: | Good in most resin systems. |
| HYDROLYTIC STABILITY: | Exposure of tris 2,3P to water at 25°C for 24 hours does not result in a detectable change in acid number. Exposure to strong caustic at elevated temperatures results in dehydrohalogenation. |
| HANDLING: | Use protective means to avoid contact with eyes, skin and clothing. Wash immediately with soap and water if contact is made. Do not take internally. |

AVAILABILITY:

| Container | Net Weight-lbs. |
|---|---|
| 1½ gal. pail | 26 |
| 5 gal. can | 87 |
| 30 gal. drum | 550 |

### 5.1.5.1 Commercial Products

The process of manufacturing a flame retarded textile product for retail sales is at the tail end of a multi-faceted production process leading from the chemical producers, to fiber producers, textile mills, and dyers and finishers.[6] Properties of the starting materials, intermediary products and the final product are all important to understand in order to completely assess the potential impact of flame retardants environmentally.

To date there is very little known about the possible decomposition products and what is likely to occur in actual use from synergistic interactions of the flame retardant with other components of the various products.

In the course of the interview phase of the study, much effort was devoted to investigating possible decomposition products and spontaneous reaction products which may occur in manufacture or by interaction with other components in the fiber and/or the finish formulations. No evidence was uncovered to indicate a threat, environmentally or toxicologically from the use of flame retardants for textiles, or textile product fills such as flexible polyurethane foams.

Rigid urethane which is not a textile component is suspect. Certain products of combustion are said to be toxic but investigation of the issue was beyond the scope of this study.

Speculative concern has surfaced with regard to a potential for interaction of hydrogen chloride and hydrogen bromide introduced by flame retardance technology with formaldehyde based finishes to form carcinogenic bis chloromethyl ether and the bromo analog.

Areas for future chemical and physical investigation that have not been reported on may require laboratory testing or legislative authority to solicit proprietary data directly from manufacturers. Some areas were addressed in this study without successful retrieval of data. Where compounds such as brominated bis phenol A, tetra bromophthalic anhydrides and even tris (2,3 dibromopropyl) phosphate are used in melt spinning of polyester or nylon fibers, very high temperatures (300-350°C) are involved and decomposition products may result. These may be precipitated in an afrerwash or they may leave oligomers and monomers unreacted on the product to be leached out during the dyeing process or end up on the final product.

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[6] Man-Made Fiber Producers Association, Inc. Man-Made Fiber Fact Book Washington, D.C., 1974, 64pp. (OTS-AA-0418).

Questions that remain unanswered are: will there be chemical changes of environmental concern occuring in normal use? For example, will they hydrolze on repeated washings? Will they oxidize on bleaching or chlorinate with chlorine bleach? How will they or their products react with exposure to sunlight, ozone, $NO_2$ and $SO_2$ in the atmosphere?

Until more is known about the specific products of decomposition these questions cannot be accurately answered.

## 5.2 PRODUCTION

Production includes these subsections:

- Producers
- Uses
- Current practice

### 5.2.1 Producers

Producers involved in the manfacture of flame retardant products include:

- Chemical Manufacturers
- Fiber Producers
- Dyers and Finishers

Producers with major investments in flame retardant compounds are provided in the following tables along with plant site locations:

Table 5-5 Chemical Manufacturers
Table 5-6 Man Made Fiber Producers
Table 5-7 Dyers and Finishers

## TABLE 5-5. CHEMICAL MANUFACTURERS

| PRODUCER | SITE |
|---|---|
| 1) American Cyanamid | Bound Brook, New Jersey |
| 2) Ciba-Geigy Corporation | Ardsley, New York |
| 3) Dow Chemical Company | Midland, Michigan |
| 4) Great Lakes Chemical Company | Lafayette, Indiana |
| 5) Hooker Chemical Company | Niagra Falls, New York |
| 6) Michigan Chemical Company | Chicago, Illinois |
| 7) Monsanto Chemical Company | St. Louis, Missouri |
| 8) Stouffer Chemical Company | Westport, Connecticut |
| 9) Tenneco Chemicals, Inc. | Piscataway, New Jersey |

## TABLE 5-6. MAN-MADE FIBER PRODUCERS

| Producers | Plant Locations and Fibers Produced |
|---|---|
| Allied Chemical Corporation<br>Fibers Division<br>One Times Square<br>New York, New York 10036 | Columbia, S.C. (nylon & polyester)<br>Hopewell, Va. (nylon and polyester)<br>Moncure, N.C. (polyester) |
| American Cyanamid Company<br>Fibers Division<br>Berdan Avenue<br>Wayne, New Jersey 07470 | Pensacola, Florida (acrylic) |
| American Enka Company<br>A Part of Akzona, Inc.<br>Enka, North Carolina 28728 | Central, S.C. (nylon & polyester)<br>Enka, N.C. (nylon & rayon)<br>Lowland, Tenn. (nylon, polyester & rayon |
| Beaunit Corporation<br>Fibers Division<br>261 Madison Avenue<br>New York, New York 10016 | Elizabethton, Tenn. (nylon, polyester & rayon)<br>Etowah, Tenn. (nylon) |
| Carborundum Company<br>P.O. Box 337<br>Niagara Falls, New York 14302 | Sanborn, N.Y. (novoloid) |
| Celanese Corporation<br>Celanese Fibers Company<br>P.O. Box 1414<br>Charlotte, North Carolina 28201 | Cumberland, Md. (acetate & triacetate)<br>Narrows, Va. (acetate)<br>Rock Hill, S.C. (acetate & triacetate)<br>Rome, Ga. (acetate) |
| Courtlauds North America Inc.<br>104 West 40th Street<br>New York, New York 10018 | Le Moyne, Ala. (nylon & rayon) |
| Dow Badische Company<br>Williamsburg, Virginia 23185 | Anderson, S.C. (nylon & polyester)<br>Williamsburg, Va. (acrylic & metallic) |
| E.I. du Pont de Nemours and Company, Inc.<br>Textile Fibers Department<br>Wilmington, Delaware 19898 | Camden, S.C. (acrylic, nylon & polyester<br>Chattanooga, Tenn. (nylon & polyester)<br>Kinston, N.C. (polyester)<br>Martinsville, Va. (nylon)<br>Old Hickory, Tenn. (olefin & polyester)<br>Richmond, Va. (aramid, fluorocarbon, nylon & olefin)<br>Seaford, Delaware (nylon)<br>Waynesboro, Va. (acrylic, acetate & spandex)<br>Wilmington, N.C. (polyester) |

TABLE 5-6. (Contd.)

| Producers | Plant Locations and Fibers Produced |
|---|---|
| Eastman Kodak Company<br>Carolina Eastman Company Division<br>Kingsport, Tennessee 37662 | Columbia, S.C. (polyester |
| FMC Corporation<br>Fiber Division<br>1617 John F. Kennedy Boulevard<br>Philadelphia, Pennsylvania 19103 | Front Royal, Va. (polyester & rayon)<br>Lewistown, Penna. (polyester)<br>Meadville, Penna. (acetate & vinyon)<br>Radford, Va. (polyester)<br>Nitro, W. Va. (rayon)<br>Parkersburg, W. Va. (rayon) |
| Hercules Incorporated<br>Fibers Division<br>910 Market Street<br>Wilmington, Delaware 19899 | Covington, Va. (olefin)<br>Oxford, Ga. (olefin) |
| Hoechst Fibers Incorporated<br>1515 Broadway<br>New York, New York 10036 | Spartanburg, S.C. (polyester) |
| Monsanto Textiles Company<br>800 N. Lindbergh Boulevard<br>St. Louis, Missouri 63166 | Decatur, Ala. (acrylic, modacrylic & polyester)<br>Greenwood, S.C. (nylon)<br>Guntersville, Ala. (nylon & polyester)<br>Pensacola, Florida (nylon) |
| Phillips Fibers Corporation<br>Subsidiary of Phillips Petroleum Company<br>P.O. Box 66, Interstate 85<br>Greenville, South Carolina 29602 | Rocky Mount, N.C. (polyester)<br>Seneca, S.C. (carpet backing)<br>Spartanburg, S.C. (olefin)<br>Guayama, Puerto Rico (nylon) |
| Rohm and Haas Company<br>Fibers Division<br>Independence Mall West<br>Philadelphia, Pennsylvania 19105 | Fayetteville, N.C. (nylon & polyester) |
| Union Carbide Corporation<br>Films-Packaging Division<br>Fibers Department<br>270 Park Avenue<br>New York, New York 10017 | South Charleston, W. Va. (modacrylic) |

## TABLE 5-7. DYERS AND FINISHERS

| MANUFACTURER | SITE |
|---|---|
| 1) Burlington Mills | Greensboro, North Carolina |
| 2) Collins and Aikman | New York, New York |
| 3) Cone Mills | Greensboro, North Carolina |
| 4) Dan River | Danville, Virginia |
| 5) Deering Milliken Corporation | Spartanburg, South Carolina |
| 6) Fieldcrest | Eden, North Carolina |
| 7) Graniteville Company | Graniteville, South Carolina |
| 8) Guilford Mills | Greensboro, North Carolina |
| 9) M. Lowenstein and Sons | New York, New York |
| 10) Reeves Brothers | New York, New York |
| 11) Riegel Textile Corporation | New York, New York |
| 12) Russell Corporation | Alexander City, Alabama |
| 13) Springs Mills | Fort Mill, South Carolina |
| 14) J.P. Stevens and Company | Garfield, New Jersey |
| 15) United Merchants and Manufacturers | New York, New York |
| 16) United Piece Dye Works | Hightstown, New Jersey |
| 17) West Point Pepperell | West Point, Georgia |

Tris (2,3 dibromopropyl) phosphate is available from Stauffer Chemical, Michigan Chemical, Dow Chemical, Great Lakes Chemical and Tenneco. While other organo-halogens and organo-phosphates are listed in the product lines as discussed in Section 5.1, tris is regarded as the only commercially significant flame retardant for man-made textile products in the civilian marketplace.

Other somewhat less significant flame retardant chemicals at present may become commercially more significant as the demand for flame retarded products grows. Brominated bis phenol A and the less important chlorinated analog is produced by Dow Chemical, Great Lakes Chemical, Michigan Chemical and Stauffer Chemical.

Diamines of polyhalogenated biphenyls are made by du Pont, Monsanto and Celanese. Tetrobromophthalic anhydride and tetra chlorophtalic anhydride are produced by Dow, Great Lakes, Michigan, Stauffer, du Pont, Rohm and Haas and Celanese.

Vinyl chloride and vinylidene chloride, in addition to being used as copolymer reactants for modacrylic or saran fibers, may be applied as fabric finishes to produce coated fabrics. The production of vinyl chloride has come under strict regulation in the United States. Companies most associated with it are Dow Chemical, Goodrich and Union Carbide.

Pyrovatex$^R$ is a product of Ciba-Geigy that is currently in development for use on cotton-polyester blend fabrics. Its effectiveness for use on 100% cotton and blends have given it a strong market position. It is reported to be the market leader, at present, for cotton use, surpassing THPC. However, it has not proved to be as effective for man-made fibers as tris 2,3 (dibromopropyl) phosphate.

To many, the dyeing and finishing operations is synonomous with textile manufacturing. There are more than fifty companies either using flame retardant fibers for the manufacture of flame retardant fabrics or treating fabrics with flame retardant finishes. The list in Table 5-7 represents the largest corporations.

The textile industry was one of five worst affected by the economic recession of 1974. For the first time in 15 years, the growth of man-made fiber output was reversed. Global output of cellulosics and synthetics fell 3% from 1973. The 1974 output equaled 11.27 million metric tons. World wide output of thermoplastic staple and filament yarns fell 2.7% to 7.53 million metric tons. Domestically, the decline of synthetic production was down 1% to 2.69 million metric tons.

At the same time, countries outside the United States, Western Europe and Japan increased fiber production by 4.2% to nearly 3.1 million metric tons, including rayon. Their thermoplastics production was up 6% and rayon 2.4%. Their overall production constitutes 27% of the total world wide market.

Globally, polyester staple and fiber gained an improved position by moving up 2.2% over 1973 to 3.24 million metric tons solely in countries outside the United States, Europe and Japan. The acrylics and polyamides slipped 8% to 1.43 million metric tons. Polypropylene and polyvinyl alcohol fibers held steady at 0.3 metric tons. The polyester fibers now account for 43% of the total. Polyamides have 34%, acrylics 19% and other classes of thermoplastics 4%.

The United States is the largest producer of man-made fibers. U.S. output exceeded 2.7 million metric tons in 1974. This was 36% of the world wide production. Polyesters made up 1.4 million metric tons. This is 52% of the total U.S. output.[7]

On a global or even total domestic output scale, the production of flame retarded textiles is less than 5% of the total. This is less than 0.3 million metric tons of flame retardant fabric. On a weight basis, flame retardant additives, coreactants and finishes make up less than 10% of the product. Therefore, the total textile flame retardant material produced is estimated at less than 0.03 million metric tons per year from all sources. Companies that have not had significant earnings in the specialty chemical marketplace or fiber manufacturing may divest themselves of flame retardant products if the trend continues. Union Carbide was the first such casualty. In November 1974 it was announced that the fiber manufacturing operation in West Virginia would be discontinued. The company gave the official reasons as feedstock shortages, high labor cost, EPA waste treatment regulations and OSHA regulations of vinyl chloride production used in its only product, modacrylic Dynel.[8]

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[7] Chemical and Engineering News. "Prospects for Fibers Continue to be Good." V. 53 (6) February 10, 1975, p. 12

The turmoil in the industry made it virtually impossible to develop accurate estimates of current and future production levels and prices.

### 5.2.1.1 Production Trends/Volume

Since the trend in textile manufacturing continues to favor the man made fibers, particularly the thermoplastic polyesters, polyamides and polyolefins (6-7 billion lbs. per year) the question to be answered is whether these will be manufactured as flame retardant fibers or whether chemical finishes will be applied in a finishing process. The impact of shortages of petroleum based feedstock *vis a vis* crop fluctuations for cotton is very uncertain for both the short and long term outlook. Still, there is no clear indication as to whether the future development of flame retardant textiles and end products will favor intrinsically modified fiber raw materials or whether the flame retardant chemicals will be applied in a fabric finishing process.[9,10]

There is conflict between government and industry as to which producer group should be responsible for meeting the flame retardance performance standard. The textile manufacturers favor looking to the fiber producer. The Consumer Product Safety Commission places the responsibility on the fabric producer and the end product manufacturer.

Because of these uncertain economic factors and since all present efforts to meet flame retardance standards have required trade offs in economy, aesthetics, wear properties and the like, it can be anticipated that intensive research to find the "ideal" product (particularly for popular cotton/polyester blends) will continue. Three approaches are being made: modification of the polymer base, the use of improved additives in fiber production and the application of finishes. All will continue to be important. It is almost certain that the ultimate answer, which many textile professionals and executives anticipate in the next five years, will require totally different chemicals than are now commonly used for thermoplastic fibers.

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[8] Personal Communications

[9] LeBlanc, R.B. What's Available for Flame Retardant Textiles Textile Industries, 138 (2): 115-120 (1974) (OTS-AA-0480).

[10] Eisenberg, B.J.; E.D. Weil A Review of Durable Flame Retardants Textile Chemist & Colorist, 6 (11): 23-27, (1974) (OTS-AA-0474).

Because of this likelihood, it will be necessary for the EPA to continue to monitor developments in the field of textile flame retardance for new chemicals and chemical classes until a truely effective flame retardant process is developed.

### 5.2.2 Uses

Use is of two kinds. First, there is the use of chemicals to produce flame retardant fibers and fabrics through coreactants and additive monomers and oligomers. Second, there is the use of finishes to impart flame retardance to fabrics used in end products. In addition, product design is an important aspect of the textile flame retardancy issue, especially as federal regulations are mostly directed at the end product.

This study has pragmatically concentrated on the production of fibers and fabrics and has only marginally been concerned with developments in product design. Certain products can be designed to meet published standards without special flame retardant fibers and fabrics. To that extent, those products are not likely to be sources of environmental concern as a result of their need to be flame retardant. For example, carpet standards FF 1-70 and 2-70 can be met by proper construction employing most pile yarns, without the need to incur additional costs for flame retardance. Matresses can meet the matress standard FF 4-72 without special finishing. Thus, mattresses are not of general concern. Automobile furnishings have tended to use more flat laid plastics and saran based upholstery.

Practically, acrylics and nylons are not effectively flame retarded by finishes. Therefore, it is more common to modify the polymer backbone and produce modacrylics and high temperature polyamides with inherent stability. This eliminates these special fibers from use in many product end uses, unless the fiber/fabric was especially produced for a specially designed retail product for a specific market, for example flame retardant, light weight nylon tents or modacrylic children's sleepwear.

### 5.2.2.1 Flame Retardant Fibers

Table 5-8 gives the list of flame retardant fibers currently available. Each of the fiber types has a somewhat different profile.

Cellulose acetate and triacetate is effectively flame retarded by adding tris-(2,3 dibromopropyl) phosphate to the material melt prior to spinning.[11] The process involves the thermal diffusion of tris by driving the tris into the fiber, under pressure dyeing. Some work is being done on a process using organic solvents to apply solution of tris onto a dyed fabric and then setting it into the fiber with dry heat. The tris is theoretically padded on at 8-10% add on by weight for polyester fabric. It is durable through 50 warm water washings. Tris will be leached out by solvent dry cleaning. It is not soluble in water.

Acrylics can also be flame retarded with tris but the usual approach is to coreact 35-85% acrylonitrile monomers with vinyl chloride, vinylidene chloride or vinyl bromide. Modacrylics are often used in blends with cotton and polyesters to achieve flame retardance in a finished fabric. The addition of small amounts of a vinyl phosphonate monomer has been used by Asalin in Japan to achieve flame retardance and improved aesthetics.

Polyester is the least costly thermoplastic fiber and it is also the volume leader. Because of this, much research is aimed at various polyester fibers and polyester blend fabrics. The problem of the polyester blend is not yet solved, and it is likely to require a finish compatable with the aftertreatment of cotton since the cotton component will always require aftertreatment. 100% polyester treatments have been successful. The flame retardant moiety used

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[11] Refer to note 6, page 5-12.

## TABLE 5-8. FLAME RETARDANT FIBERS

| Fiber | Company | Chemical Nature | Composition of Fabrics | Comments and Major Markets |
|---|---|---|---|---|
| Acele FLR (TM) | Du Pont | Acetate with TDBPP additive | 100% acetate and blends with up to 20% polyester | Apparel |
| FR Acetate | Celanese | Acetate with TDBPP additive | 100% acetate and blends with up to 20% polyester | Apparel |
| Sayfr (TM) | FMC | Acetate with TDBPP additive | 100% acetate and blends with up to 20% polyester | Apparel |
| Arnel FR (TM) | Celanese | Triacetate with TDBPP additive | Blends with polyester | Apparel |
| Dacron 489 (TM) | Du Pont | Polyester copolymer with ethoxylated tetrabromobisphenol | 100% polyester and blends | Developmental product |
| HEIM (TM) | Toyobo Co. | Polyester containing aromatic, sulfur-containing phosphonate | | Semi-commercial |
| Extar FR (TM) | Teijin Co. | Bromine containing polyester | | Developmental products |
| Orlon FLR (TM) | Du Pont | Modacrylic | | Developmental product |
| SEF (TM) | Monsanto | Modacrylic | 100% SEF and blends with acrylic or polyester | Apparel, drapery and industrial fabrics |
| Verel (TM) | Eastman | Modacrylic | 100% Verel and blends with rayon or acrylic | Apparel, drapery, carpet and others |
| Dynel (TM) | Union Carbide | Modacrylic | 100% Dynel and blends | Apparel, carpet and others |

## TABLE 5-8. (CONTINUED)

| Fiber | Company | Chemical Nature | Composition of Fabrics | Comments and Major Markets |
|---|---|---|---|---|
| Leavil (TM) | Montedison | Vinyon | 100% Vinyon and blends with polyester or cotton | Apparel, drapery and others |
| Clevyl T (TM) | Rhone Poulenc Textile | Vinyon | 100% Vinyon and blends with polyester or cotton | Apparel, drapery, carpet, and others |
| Valren (TM) | Teijin | Vinyon | 100% Vinyon and blends with polyester or cotton | Apparel, drapery |
| Cordelan (TM) | Kohjin Co. | Vinal-Vinyon Matrix | 100% Cordelan and blends with up to 20% of cotton or polyester | Apparel |
| Avril PFR (TM) | FMC | Rayon with a Phosphazene derivative added | 100% rayon and blends with fibers such as Nomex | Safety apparel, aircraft upholstery and others; Developmental product |
| Bell Flame FR (TM) | Kanebo Co. | Rayon with FR additive | | Developmental product |
| Wool | | Protein | 100% wool and blends with Fiberglas, Vinyon, Nomex, etc. | Apparel, industrial work clothes, aircraft upholstery and others |
| Fiberglas (TM) | Owens-Corning | Glass | 100% Fiberglas and blends | Drapery, industrial work clothes and others |
| Nomex (TM) | Du Pont | Aramid (Aromatic Nylon) | 100% Nomex and blends with Kynol, Wook, etc. | Apparel, industrial fabrics & airline upholstery |
| Kynol (TM) | Carborundum | Phenolic-based | 100% Kynol and blends | Industrial fabrics; semi-commercial product |

must be thermally stable at temperatures exceeding the 300°C baths needed in melt spinning processes. Tris is not recommended above 350°C. The most useful compounds have been 2,5 dibromoterephthalic acid from Amoco Chemicals and Tetrabromobisphenol A.[12]

Nylon, aside from the aramids, has not been satisfactorily flame retarded with simple additives or coreactants. In fact, in nylon, 6 some bromine additives can increase flammability by causing a more rapid deterioration to the caprolactam monomer. Nylon 66 has been treated with limited results with polybromobiphenyl and polybromodiphenyl oxide.

Polyolefins have a need for an effective treatment for use in carpets, curtains, and tenting. Moieties that have reached the semi-commercial stage of development are a Cities Service product that is bicyclic with bromine and chlorine attachments to the rings, and a Phillips Petroleum hexabromide of dicyclohexenylethylene.

### 5.2.2.2 Flame Retardant Finishes

Although we can expect improved fiber modification and increased consumption of flame retardant fibers in the future, there will always be an important proportion of all flame retardant fabrics, especially blends that will be treated by the dyer and finisher. Chemical companies seem to be more interested in developing new chemicals for use by the textile producers than the fiber producing industry.

Tris (2,3 dibromopropyl) phosphate is being used with limited success as a fabric finish for polyesters, nylons and acrylics. Two techniques are available. The conventional pad-dry application with heat fixation is most commonly used on woven fabric. The tris is generally applied in an aqueous emulsion and deposits 5-10% add on. The treated fabric is dried at high heat, quickly and the residue is removed by afterwash scouring.

Cotton/polyester fabrics have been treated with Ciba-Geigy's Pyroatex. However, there are conflicting reports about its effectiveness for blends containing more than 25% polyester fiber. Adverse effects to the fabric hand and weight have also resulted.

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[12] Refer to note 10, page 5-20.

The role of the dyers and finishers in flame retarding man made textiles will depend on several factors:

1. The rate at which compulsory regulations from the Consumer Product Safety Commission will increase the demand for flame retardant fibers beyond the capacity of the fiber producers to produce. (This is the current situation for the modacrylics, polyester and triacetate.) As a result, most polyester fabrics and a considerable amount of nylon is being treated by the dyer-finisher.

2. The degree to which the fiber producers can impart flame resistance to generic fiber type without detracting from the other desired properties expected of these fibers in the end-use performance. Chemical modification of fibers to impart flame retardancy often influences dyeing properties, whiteness, thermal stability and mechanical properties.

3. The degree to which chemicals become available for more effective and more economical application in dyeing and finishing. Thus, if chemicals become available which are selectively substantive onto the specific fibers during the dyeing operation this will significantly reduce cost and improve effectiveness.

4. The degree to which the present blend levels of polyester/cotton (65/35, 50/50) and polyester/wool (55/45) remain the major blends. For example, there are already a group of blended fabrics, 75 - 80% modacrylic with 25-30% Of cotton, which pass sleepwear standard FF-5-74. 65% cotton-35% polyester can be finished as flame retarded fabrics. Cotton, Inc. recently announced a finish which when applied to a 60/40 cotton/polyester fabric resulted in durable flame retardancy. This is not true of the 65%PE-35% cotton blend.

### 5.2.3 Current Handling Practices

Points of contact where handling practices are of concern include the manufacture, shipping and handling of the flame retardant chemicals, the fibers and the retail products in the home. In use, melt spun fibers (nylon and polyester) may contain a small amount of oligomer which leaches off in washing. The chemical additives to the man-made fibers will leach off in washing very slowly, e.g., less than 40% of total in 50 wash cycles which amounts to less than a .1% chemical per wash. It is not known what the chemical reaction is of oxygen and chlorine bleaches with the particular fibers and chemical additives and whether the resultant oxidized or halogenated additive represent hazards of dermatitis or toxicity through contact or ingestion.

Since the advent of permanent press fabrics, consisting of chemical cross-linking cotton in blends with polyester, all washing machine cycles have trended toward lower and lower washing temperatures. Very little hot water today enters the washing machine at higher than 65°C and most washing is carried out at the warm setting which is between 40-50°C. We no longer boil clothes and relatively little of the family wash goes to the commercial laundry.

In any event, the product data safety sheets of the chemical manufacturers and expert opinion solicited in the course of the project indicated that no extraordinary measures were necessary in the handling of common textile flame retardant materials. Typical precautions were advised: avoid contact with skin, eyes and clothing. In case of contact, wash immediately with soap and water. Do not take internally. In case of ingestion, induce vomiting.

## 5.3 ENVIRONMENTAL EFFECTS

The predicted increase in requirements for flame retardant textiles will increase the production volume of these materials, and thus the potential environmental hazards. Pollution could emanate from several sources:

- textile production and finishing mills
- laundering of flame retarded products
- disposal of the finished materials

The textile industry is concentrated primarily in the southeastern U.S. and produces a large diversity of waste products. These waste effluents appear both in the atmosphere and in waterways. Each of the waste products require treatments tailored to the specific waste.[13] In addition to water and air pollution, solid waste disposal must be considered.

### 5.3.1 Chemistry Involved

In general, the flame retardant substances are relatively stable and thus pose no overt environmental hazards in themselves. However, under conditions of exposure to ultraviolet light and extreme heat, decomposition occurs. Further, unreacted monomers, oligimers, platicizers, and the like may be present in the flame retardant material which, unlike the base material are reactive and have a different chemical profile. They can pose a potential environmental threat. For example, the melamine/formaldehyde resins, which are used in flame retardant finishing operations are innocuous in themselves. However, they do allow finite amounts of formaldehyde to be liberated during the drying and curing operations. Some may be liberated from finished products as well. In the presence of chloride ions, commonly associated with flame retardants, the concern is far greater than with either the formaldehyde or chloride alone. Formaldehyde is known to react with chloride to yield bis (chloromethyl) ether (BCME), a known carcinogen:

$$2\,Cl^- + 2_2CHO + 2H^+ \rightleftharpoons ClCH_2OCH_2Cl + H_2O$$

This material causes lung cancer in rats on exposure to levels of 100 ppb in the air for several months[14], and could thus pose a serious atmospheric contamination problem.

Another class of potential additives, the polychlorinated biphenyls, are environmental contaminants which have been reported in air, water, sediment, and food chain samples.[15] These compounds have been shown to produce lesions in various animals and to induce pathologic changes in rhesus monkeys.[16]

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[13] Kornegay, Billy H. Textile Wastes. J. Water Pollution Control. Fed. 46 (6): 1286-1290, (1974) (OTS-AA-0450).

[14] Hurwitz, Melvin Rohm & Haas. Assessing the Hazard from BCME in Formaldehyde-containing Acrylic Emulsions. Amer. Dyestuff Reporter, 63 (3): 62-64&77 (1974) (OTS-AA-0457).

[15] Eichelberger, James W.; W.L. Budde, L.E. Harris Analysis of the Polychlorinated Biphenyl Problem Analytical Chemistry, 46 (2): 227-232 (1974) (OTS-AA-0455).

[16] Abrahamson, L.J.; J.R. Allen The Biological Response of Infant NonHuman Primate to a Polychlorinated Biphenyl. Environmental Health Perspectives. Exp. (4): 81-86 (1973) (OTS-AA-0441).

Structurally, there are molecular similarities between organophosphorus flame retardants and agricultural products, and between organochloride flame retardants and pesticides. However, these superficial similarities can be misleading. Molecular modifications of a very minor type can produce gross changes in biological activity or inactivity. Hence, it is not surprising that the toxicity of the flame retardants under review was seen to be low.

### 5.3.2 Biology Involved

The absorption, distribution, metabolism, and excretion of the flame retardant materials, their decomposition products or their starting materials have not received extensive study. Indeed, our intensive literature search revealed no studies in either laboratory or uncontrolled situations. Toxicity data, however, has been collected. This is described in the next section.

### 5.3.3 Biodegradation

Biodeterioration is the breakdown of a material by living organisms. It can occur in three ways: a colony of microorganisms may feed on detritus which is on the surface of the material; rats or other organisms may mechanically gnaw or tear at the material; or biochemical attack by microorganisms may occur. Polymers and plastics are unique among waste materials in that they resist all three forms of biodegradation. They especially resist attack by microbial enzymes, and it is doubtful that a mutant organism will emerge which has an enzyme system capable of degrading synthetic, thermoplastic polymers.[17]

Activated sludge is recommended as the best practical control technology for treatment of textile mill waste treatment, including mills whose operations include flame retardance. However, such a process is of little value when the waste products are non-biodegradeable.[18] For such materials, recovery of energy or useful products may be more practical through pyrolysis or incineration with steam recovery.

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[17] Mills, John The Biodeterioration of Synthetic Polymers and Plasticizers. CRC Critical Reviews in Environmental Control, 4 (3): 341-351 (1974) (OTS-AA-0449).

[18] Ameen, Jospeh S. How the Effluent Guidelines Affect You. Textile Industries, 138 (10): 36,37,38,39, & 41 (1974) (OTS-AA-0481).

The biodegradability of tris (2,3 dibromopropyl) phosphate was determined in one study.[19] A microbial innoculum was taken from raw sewage, and the test sample was matched against a blank containing no innoculum and a control containing the innoculum and linear allkylated sulfonate (LAS), but no tris. Bromine content of the liquor of each of the test solutions was measured at 0, 5, 10, and 15 days. Allowing for the normal solubility of tris in water (1.6 ppm), an amount of tris equal to 2.4 times the dissolved tris was degraded in 5 days. Thus, the tris was broken down by the microorganisms in the raw sewage.

### 5.3.4 Radiation and Thermal Decomposition

Dupont Nomex$^{R}$ is degraded by ultraviolet waves of natural and artificial light. Results of exposure include discoloration and loss of tear strength.[20] This yellowing effect causes some loss in the reflective qualities of the material, which may be related to a decrease in tear strength and an increase of burning rate (in inches/min.) as a result of exposure to light.[21] Long-term exposure to sunlight may result in similar degradation of other flame retardant chemicals, but studies have not been performed to indicate this.

Thermogravimetric analysis (TGA) combined with mass spectroscopy (MS) has proved a useful tool for identification of polybenzimidazoles. The TGA curve shows weight loss when a given temperature is attained and the MS provides the composition of gasses given off. When thermal decomposition of the PBI's takes place in the presence of air, water and $CO_2$ are the primary degradation products. Further decomposition results in the production of carbon monoxide.[22]

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[19] Kerst, Fred A. Toxicology of Tris(2,3 dibromopropyl) Phosphate. Unpublished manuscript, Sept. 20, 1974 (OTS-AA-0435).

[20] E.I. du Pont de Nemours & Co., Inc. Properties of Nomex® High Temperature Resistant Nylon Fiber. N-236, Wilmington, Del., Dupont Technical Information Bulletin, 12 pp (1969) (OTS-AA-0421.

[21] Day, M.; D M. Wiles Effect of Light on the Flammability of Nomex Fabric. Textile Research Journal, 44 (11): 888-891 (1974) (OTS-AA-0487).

[22] Tsur, Yoel; Y.L. Freilich, M. Levy TGA-MS Degradation Studies of Some New Aliphatic-Aromatic Polybenzimidazoles. Journal of Polymer Science (Poly Chem), 12 (7): 1531-1539 (1974) (OTS-AA-0452).

Another study[23] applied the same TGA-MS technique to a PBI sample in an argon atmosphere and to a Nomex sample. Again, the first step of weight loss of the PBI was attributed to water, with the same result for Nomex. No appreciable amounts of other evolved gasses from the Nomex sample up to 405°C were found. The authors concluded that these data did not give rise to any particular concern with respect to the usage of these two materials, particularly in applications as materials for interiors of passenger and cargo aircraft.

The combustion of flame retardant materials, in general, gives rise to a variety of thermal degradation products, including formaldehyde and (particularly for the chlorinated polymer products) hydrogen chloride and other breakdown products. Heat may also result in the production of bis-chloromethyl ether (BCME), which is carcinogenic. The concern for this event should be minimal in the case where an accidental fire occurs. However, in chronic situations, such as incinceration, the presence of these products and their environmental effects should be investigated.

The Environmental Protection Agency has recently approved the incineration of chlorinated hydrocarbon wastes, resulting from Shell Oil Company's production of glycerine, allyl chloride, epichloride, and vinyl chloride, aboard the special incinerator ship Vulcanus in the Gulf of Mexico. Surface monitoring at 1000 feet behind the vessel showed a concentration of 1 ppm hydrogen chloride. No detectable changes in environmental stress were noted, although both phyto and zooplankton were monitored.

The primary hazard in all acute fire situations is the presence of carbon monoxide in lethal doses. The amount of carbon monoxide formed is proportional to the carbon content of the burned material. When organic materials are burned, sufficient carbon monoxide can be produced to be lethal.

Nitrogenous organic substances, such as nitrile plastics, produce cyanide upon combustion. As little as one percent cyanide in breathing air can result in death in 20 minutes.

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[23] Kleinberg, Gerd A.; D.L. Geiger Tandem Thermogravimetric Analyzer -- Time-of-flight Mass Spectrometer System Designed for Toxicological Evaluation of Nonmetallic Materials. AMRL-TR-71-71, Wright-Patterson A.F.B. (OTS-AA-0514).

### 5.3.5 Bioaccumulation

The stable chlorinated molecules, when introduced to the food chain, accumulate in various organs of animals and produce reproductive hazards. These stable compounds also have tumorigenic potential. It is quite likely that stable bromo and iodo analogs have qualitatively similar behavior, although most of the research has been performed on the chlorinated compounds.

A recent incident involving poly-brominated biphenyls demonstrated the proclivity of these materials, when ingested, to be passed on in dairy cattle through milk used for human consumption. Farm Bureau Services, Battle Creek Michigan, unknowingly blended this (non-textile) fire retardant chemical with animal feed in place of magnesium oxide, a nutrient additive. Extensive laboratory testing and research by state, U.S. Department of Agriculture, Food and Drug Administration, and private laboratories resulted in seizure of lots of butter and cheese containing the polybrominated biphenyls. Tons of milk from quarantined dairy herds were destroyed. Possible effects of the biphenyls on human health are under investigation by the Michigan Department of Public Health.

Polychlorinated biphenyls (PCB) are used in flame retardant mixtures, such as polyolefin yarns. Various studies have been undertaken to show that measurable amounts of PCB's may be found in human and cow's milk as well as in human adipose tissue. PCB's have been blamed for premature births and early deaths in California sea lion pups, and breeding mink and their offspring have been shown to be sensitive to these compounds.[24]

Stable compounds such as tris (2,3 dibromopropyl) phosphate will tend to accumulate in trash dumps and other disposal sites, resulting in environmental, rather than biological accumulation. It is not likely that tris will be readily degraded by the effects of weather or other environmental agents, due to its relative stability.

Tissue residue analysis of rats fed tris (2,3 dibromopropyl) phosphate for a period of 28 days at levels of 100 ppm and 1000 ppm have shown dose related high residue levels in the muscle, liver, and fat of the test animals, although no histopathological effects were noted. Bromine levels in these tissues were determined using the neutron activation technique. After six weeks withdrawal, residue levels essentially disappeared, with bromine levels from the dosed animals returning to the normal background levels of the control animals.[25] These data demonstrate the stability of the brominated organophosphorous flame retardant in a biological system.

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[24] Refer to note 16, page 5-28.

Chlorinated polymers are likewise stable in themselves, but carry the potential for presence of unreacted monomers and oligimers. When these highly reactive compounds leach out of the polymers, they pose toxic and carcinogenic hazards, if they are not effectively degraded in the environment. However, it is purely speculative as to whether these oligimers and monomers will enter the food chain.

### 5.3.6 Environmental Transport

Studies of environmental transport of substances related to those included in this report have been somewhat limited, but provide a model for future research. For example, one paper[26] discussed results of sampling the waters of the Northwestern Atlantic Ocean with a plankton net. Samples of various types of plastics were recovered, none of which were toxic. At the same time, they are not biodegradeable. Samples of plastic particles have been found in the digestive tracts of various marine species. While these particles are non-toxic, they may lead to intestinal tract blockage and possible mortality in larval fishes.[27]

Other investigators measured PCB concentrations in the atmosphere over the western North Atlantic and concluded that the PCB concentrations in the atmosphere decrease exponentially with the distance from land. Thus, wind transport is the major source of chlorinated hydrocarbons in the oceans.[28]

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[25] Refer to note 19, page 5-30.

[26] Colton, Jr., John B.; F.D. Knapp, B.R. Burns Plastic Particles in Surface Waters of the Northwestern Atlantic. Science, 185 (4150): 491-497 (1974) (OTS-AA-0445).

[27] Ibid.

[28] Harvey, G.R.; W.G. Steinhauer Atmospheric Transport of Polychlorinated Biphenyls to the North Atlantic. Atmospheric Environment, 8 (8): 777-782 (1974) (OTS-AA-0456).

However, the incineration of chlorinated hydrocarbon wastes at sea by the Vulcanus, which exceeds in 99.9% combustion, results in no evidence of organic chlorides in the sea water at the detection level of 25 ppb.

### 5.3.6.1 Monitoring and Analysis

Eichelberger and co-workers[29] suggest a method for monitoring of contaminants such as PCB's in the environment. This "subset data acquisition" technique employs a computer-controlled quadripole mass spectrometer to sample specific ions, sequences of ions, and varying dwell times of each. This technique was applied to an environmental sample from Ground Lake, St. Mary's, Ohio, and found suited to the analysis of the many isomers of PCB's. The authors conclude that this technique is clearly adaptable to analysis of other environmental pollutants, where increased sensitivity permits clear observation of molecular ions from saturated aliphatic hydrocarbons.

### 5.3.7 Unreacted Monomers

As previously mentioned, the halogenated polymers, when introduced to the environment, have the potential of giving off reactive monomers and unreacted oligomers into the soil and effluent streams. This problem is a relatively small one, considering the amounts of these compounds in finished materials. The hazards exist only when the unreacted materials, such as vinyl chloride are either tumorigenic or teratogenic. Toxic potential for natural flora and fauna due to leaching of unreacted monomers from PVC-like material is negligible. Further, since these compounds are reactive, there is little possibility for bioaccumulation. However, it is not known whether they will react with organic materials, which then become part of the food chain or whether they will introduce altered viruses or chemically altered information into plants and then into animals and ultimately into man.

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[29] Refer to note 15, page 5-28.

### 5.3.8 Waste Treatment Problems

The 1972 Amendment to the Federal Water Pollution Control Act (PC 92-500) requires textile plants which are points of discharge to navigable streams to:

A. Meet the national goal of zero discharge by 1985

B. Provide Level I Treatment (Best Practical Control Technology Currently Available) by 1977

C. Provide Level II Treatment (Best Available Technology Economically Achievable) by 1983

D. Operate under National Pollutant Discharge Elimination System Permits with designated monitoring and reporting procedures

For textile plants which discharge into municipal sewers, the Act requires pretreatment of non-compatable waste discharges, flow equalization, and neutralization; and repayment of Federal funds on the basis of waste load, including volume discharge.

On July 5, 1974, EPA published Effluent Limitation Guidelines for the textile industry pursuant to the provisions of Section 301 of the Act (Federal Register, Vol. 39 No. 130, July 5, 1974). These provide limitations on effluent loads based upon in-plant process production, including flame retardance.[30,31,32]

Many of the flame retardants are applied to textiles as finishes, utilizing the padding method. This method results in a small volume of effluent which, as in the case of the formaldehyde melamine resins, can be of an undesireable nature. As a remedy, these finishes can be applied from solvent using closed systems. In fact, synthetic fibers are better suited to solvent processing.[33]

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[30] Refer to note 18, page 5-29.

[31] Masselli, Joseph W.; N.W. Masselli, M.G. Burford Let's Try 90% First. Textile Industries, 138 (10): 32,33,35&145 (1974) (OTS-AA-0482).

[32] Anon. Effluent Guidelines Issued. American Dyestuff Reporter, 63 (8): 26&58 (1974) (OTS-AA-0468).

[33] Davis, W.S.; J. Park Practical Steps to Reduce Pollution From the Textile Industry. Textile Institute & Industry, 12 (8): 241-243 (1974) (OTS-AA-0483).

Michigan Chemical Company, the largest producer of tris (2,3 dibromopropyl) phosphate recommends disposal of this compound from finishing afterbaths in the following manner: Since tris is of low solubility, it precipitates from the afterwash solution. This precipitate is then removed from the afterwash vessel, and either incinerated or recycled.

The National Bureau of Standards vertical flame test for fabric flammability was developed at a time when most U.S. laundry detergents contained 50% sodium tripolyphosphate. NBS selected 50 launderings and tumble-dryings as the durability requirement for flame retardant garments. Since that time, phosphorus-containing detergents have been replaced by those containing carbonates. When flame retardant garments are laundered with carbonate detergents, they will often fail the vertical flame test in less than 50 launderings due to alkaline hydrolysis, ion exchange, and/or deposition of calcium carbonate. Leblanc argues[34] that, while the phosphate detergents were banned because of their eutrophication effects on lakes and other waters, these account for less than 20% of the total phosphate runoff into lakes and streams. Over half comes from agricultural and natural sources. The other half comes from sewage, which is about equally divided between detergent and human waste. Even if all this sewage were treated for phosphate removal, no one knows whether eutrophication would be significantly alleviated, because fertilizer and natural phosphate runoff into lakes may be sufficient to achieve the proper nutrient balance to continue algae growth at the current level. By the same token, the phosphate contribution of flame retardants such as tris (2,3 dibromopropyl) phosphate should be insignificant.

## 5.4 TOXICITY

The primary concerns for toxicity of flame retardant agents used in garments such as children's sleepwear or work clothes are those of contact irritation and solubility in such matrices as saliva, urine, and infantile bowel movements, then systemic absorption of the dissolved material. As will be discussed below, the compounds under review in this section have demonstrated almost no skin irritancy. Further, oral doses of tris (2,3 dibromopropyl) phosphate have been administered to rats and shown to be of very low toxicity, with the lowest published lethal dose of 300 mg/kg (Toxic Substances List, 1974 Edition). In general, commercial flame retardants were found to be of very low acute toxicity. However, no data have been retrieved regarding long term or tumorigenic effects of the flame retardant compounds.

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[34] LeBlanc, R.B. Detergents, Water and Flammability Standards: The Need to Bring Order Out of Chaos. American Dyestuff Reporter, 62 (10): 72,74,75,76, 77 & 93 (1973) (OTS-AA-0462).

### 5.4.1 Toxicology Studies of Tris (2,3 Dibromopropyl) Phosphate

Laboratory studies[35,36] of tris (2,3 dibromopropyl) phosphate indicate that this material is of very low oral and dermal toxicity, is not a skin or eye irritant, and has a low order of subacute toxicity, as determined by 28-day rat feeding studies.

#### 5.4.1.1 Oral Toxicity in Rats

Rats were dosed at 5 dosage levels and observed for mortality and weight loss in the Kerst study[37]. Table 5-9 summarizes the results:

TABLE 5-9. RESULTS OF ACUTE ORAL TOXICITY STUDY IN RATS

| Dosage Level (g/kg) | Mortality (No. Dead/No. Dosed) |
|---|---|
| 1.98 | 0/5 |
| 3.15 | 0/5 |
| 5.00 | 3/5 |
| 7.94 | 4/5 |
| 12.50 | 5/5 |

Surviving rats at 5.00 and 7.94 g/kg levels were observed to exhibit less than normal body weight gain, as did one rat dosed at the 1.98 g/kg level. $LD_{50}$ was calculated to be 5.24 g/kg.

These data tend to agree with the second study[38] where the acute oral $LD_{50}$ value in rats was calculated to be greater than 5.0 g/kg.

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[35] Refer to Note 19, page 5-30

[36] Tenneco Chemicals, Inc., Tris (2,3-dibromopropyl) phosphate-Proprietary Reports, 11 pp. (OTS-AA-0432)

[37] Refer to Note 19, page 5-30

[38] Refer to Note 36, page 5-37

### 5.4.1.2 Dermal Toxicity

Results of patch tests in both normal and abraided skin of rabbits showed no signs of dermal irritation and no mortality at a dose of up to 8g/kg. According to the Food and Drug Administration, compounds producing combined averages of 2 or less on the primary irritation index scale are classified as "mildly irritating". Tris was found to have a primary irritation index of 0.3.

### 5.4.1.3 Eye Irritation

The two independent studies each tested for eye irritation by application of the tris (2,3 dibromopropyl) phosphate to the eyes of six albino rabbits. Rabbits were observed for changes in the cornea, iris, palpebral conjunctiva. No effects were noted in any of the animals.

### 5.4.2 Human Toxicity

Human studies of tris (2,3 dibromopropyl) phosphate have taken the form of insult patch tests and both simulated and actual human saliva dissolution extraction tests. Manufacturer safety data provide special protective information on this and other flame retardants.

### 5.4.2.1 Insult Patch Tests

Fifty-two human subjects completed a patch test for skin irritation. Fifty showed no adverse reactions. Ten patches were applied to the upper arm over a 24 day period, and a single challenge patch was applied 14 to 21 days later. Of the two instances where reactions were exhibited, neither could be directly attributed to applications of the test material.

It was concluded that tris (2,3 dibromopropyl) phosphate did not produce primary skin irritation, skin fatigue or skin sensitization in the subjects tested.[39]

### 5.4.2.2 Saliva Dissolution Studies

Since infants and small children tend to suck pillows and sleepwear which may have been treated with flame retardant material, such as tris (2,3 dibromopropyl) phosphate, several independent studies have been undertaken to determine the extent to which tris or its dissolution products will leach out of treated material and thus pose both acute and longer term oral ingestion hazards.

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[39] Refer to Note 19, page 5-30

In one study[40], extraction tests were carried out by incubation of test samples for 72 hours with water at various pH levels and a simulated saliva solution, prepared for laboratory use. Extracts were found to contain low amounts of sodium bromide or hydrobromic acid, but the phosphate was not found in any extract.

One limitation of this study is the fact that although the simulated saliva solution was prepared to match the pH of natural human saliva, it did not contain such enzymes as amylase, which occur in human saliva. Therefore, brominated phosphates were subjected to natural human saliva in a study reported by Rieders.[41] The bromide content in the saliva at the completion of the experiment was found to be small. Increasing temperature increased the solubility somewhat.

No data on the solubility of flame retardants in other matrices, such as urine, perspiration infantile bowel movements, were retrieved. It is not known whether the presence of urine will either affect irritancy or solubility of the components of the flame retardants and whether they will then be absorbed through the skin.

### 5.4.2.3 Manufacturer Safety Data

Specification sheets[42,43] prepared by tris (2,3 dibromopropyl) phosphate supplies provide the following safety precautions for handling of this compound during finishing operations:

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[40] Refer to Note 36, page 5-37

[41] Personal Communication

[42] Michigan Chemical Corporations, Material Safety Data Sheet Firemaster$^{R}$ LV-T23P, Chicago, Illionois, 2pp. (OTS-AA-0430)

[43] Tenneco Chemicals, Inc., Intermediates Division; Material Safety Data Sheet Nuogard$^{TM}$, Piscataway, New Jersey, 2pp. (OTS-AA-0431)

- Health Hazard Data

  1. Eye Contact

     Flush eyes immediately with water for at least 15 minutes, and, if irritation persists, get medical attention immediately.

  2. Skin Contact

     Wash skin with soap and water. Remove contaminated clothing and wash before reuse.

  3. Oral Ingestion

     If swallowed, induce vomiting

  4. Inhalation

     If inhaled, move to fresh air.

- Special Protective Information

  1. Respiratory Protection

     None generally required. For hot vapors, use respirator.

  2. Ventilation

     Local exhaust required for hot vapors. Mechanical ventilation acceptable at room temperature.

  3. Protective Gloves

     Rubber or leather gloves required

  4. Eye Protection

     Use chemical safety goggles for splash; face shield if hot.

These are general safety precautions advised by major chemical companies for the most innocuous products. Both Tenneco and Michigan Chemical report that their highgrade tris product for flame retardant use is not a known hazardous material. Regular grade products for other uses can be a problem as a result of volatile contaminants.[44]

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[44] Personnel Communication

### 5.4.3 Toxicity to Birds and Mammals

The organophosphorus compounds, under certain conditions, such as thermal combustion, exposure to sunlight, weathering, etc. have the potential for degrading into toxic phosphines or phosphides, which are hemolytic agents with toxic properties similar to those of yellow phosphorus. However, the organophosphorus flame retardants are extremely stable and we have found no evidence to indicate that these decomposition products occur under natural conditions.

Due to the potential increase in the use of these compounds, however, some consideration should be given to investigation of the potential for phosphine/phosphate production. Phosphorus, phosphines, and phosphides are general, indiscriminate protoplasmic toxins and they will attack any cells with which they come in contact. Thus, once they enter the circulatory system, they cannot only cause hemolysis, but they can also damage any tissues and organs through which the contaminated blood flows, including bone.

These types of compounds are unstable, so that they would be toxic only to the primary contact species, such as rats in a municipal dump, but they would not be carried further in a food chain. Further, they are subject to rapid degradation, so that they do not pose either cumulative hazards or runoff hazards from soil.

Subacute toxicity studies of tris (2,3 dibromopropyl) phosphate were performed in rats[45]. The compound was fed for four weeks to male weanlings at dietary levels of 100 ppm and 1000 ppm. Body weights, feed consumption, and clinical studies were performed, and compared with negative controls. Rats at both dose levels exhibited decreases in body weight, attributed in part to decreased feed consumption. However, the slightly poorer feed efficiency of the high dose (1000 ppm) test group indicate a possible toxic effect. Body weight differences between the test and control groups lessened or disappeared during withdrawal. Hematology, blood chemistry, and urine analysis showed no untoward changes. Reduced organ weights of the test animals were attributed to decreased feed consumption, as noted above. These results do not appear to indicate any cause for alarm regarding phosphorous toxicity.

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[45] Refer to Note 19, page 5-30

The toxic effects of halogenated organic compounds upon lower animals are different from the phosphine/phosphide effects. Halogenated alkanes are likely to present a long term presence in a form which can be biologically damaging to the environment. The chorinated molecules accumulate in the lipid tissues, and they have been related to carcinogenicity (e.g., vinyl chloride and vinylidine chloride) and to adrenal cortical changes with resultant hormone and metabolic anomalies. Changes in calcium metabolism attributable to chlorinated molecules have resulted in bird egg fragility. Reproductive changes have been observed in lower animals.

One study[46] showed that infant rhesus monkeys, when subjected to doses of polychlorinated biphenyls (PCB) which produce extreme morbidity in adult monkeys, were able to survive without exhibiting any overt symptoms of PCB intoxication. The investigators hypothesized that the tissues of the infant monkeys are unable to store the PCB's as readily as are the tissues of the adult monkeys. Since the major storage depot for absorbed PCB's is adipose tissue and the infant monkey has little fat, there are fewer cells in which the compounds may be stored. A second depot are the membranes of the hepatic endoplasmic reticulum. Here again, the storage capacity of the infant monkeys would not be as great as that of the adult, since the infant monkey liver shows only minimal proliferation of hepatic endoplasmic reticulum.

In spite of these facts, we have not been able to determine that the halogenated organic flame retardants give rise to any carcinogenic or otherwise toxic substance, either in their finished state or through degradation, including combustion. The primary concern, then, is that in an acute situation, such as a fire will produce toxicants, so that survival from the carbon monoxide and any burns which may occur may be followed by sequelae.

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[46] Anonymous; Emerging Technology of Chlorinolysis, Environmental Science and Technology, Vol. 8 (1): 18-19 (1974) (OTS-AA-0444)

### 5.4.4 Lower Animal Forms

The PCB's have been found to be very stable. Much of the data that refer to DDT in the environment have been shown, through the use of newer, more sensitive analytic techniques, to actually refer to PCB's. Some DDT recently found in polar bears was shown to be PCB's rather than DDT.

One study[47] was undertaken to determine acute toxicity of the PCB Archlor 1016 in flowing sea water to the American oyster (*Crassostrea virginica*), brown shrimp (*Penaeus aztecus*), grass shrimp (*Palaemonetes pugio*) and pinfish (*Lagodon rhomboides*). The study also investigated the chronic toxicity, to uptake and retention of the PCB by pinfish. Arochlor 1016 was found to be acutely toxic to all species tested. Shell growth in oysters was greatly inhibited by exposure to 100mg per liter for 96 hours. All animals accumulated Arochlor 1016. Toxicity of Arochlor 1016 to juvenile pinfish was greater in tests lasting 6 weeks than in 96-hour exposures.

The possibility of stable chlorinated organic flame retardants leaching out of treated fabrics through laundering, or exposure to weather when disposed of, may exist, thus posing a potential hazard to lower life forms. However, there has not been any evidence of such occurrences to date, so such assumptions are purely speculative.

### 5.4.5 Microorganisms

There have been no studies of the effects of flame retardants upon microorganisms. However, the current trend toward cold water laundering brought about by the increasing amounts of permanent press fabrics and cold water detergents, have resulted in potential for bacterial retention. The use of chlorine bleaches in amounts as little as 25 ppm of chlorine in the wash cycle will kill bacteria at any temperature. Further, increased drying temperature will eliminate any residual bacteria.

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[47] Hansen, D.J.; P.R. Parrish, J. Forester; Aroclor 1016: Toxicity to and Uptake by Estuarine Animals, Vol. 7 (3): 363-373 (1974) (OTS-AA-0442)

# TABLE OF FIRE RETARDANT CHEMICALS

| | |
|---|---|
| A. | Ammonium Salts |
| A.1 | Ammonium Sulfamate |
| A.2 | Ammonium Phosphates |
| A.3 | Ammonium Phosphates with Boric Acid and Ammonium Sulfate |
| A.4 | Diammonium Phosphate; Dicyandiamide; Hexamethylene Tetramine |
| A.5 | Ammonium Phosphates; Urea |
| A.6 | Ammonium Bromide |
| A.7 | Ammonium Chloride |
| B. | Borates |
| B.1 | Boric Acid-Polyhydroxy Alcohol Condensation Products |
| B.2 | Boric Acid; Alkali metal fluorides |
| B.3 | Fluoborate treatment of asbestos - cotton fabric |
| B.4 | Boric Acid; Sodium Borate |
| C. | Antimony & Titanium Metal Oxides |
| C.1 | Antimony Oxide |
| C.2 | Antimony Oxide; Polyvinyl Chloride |
| C.3 | Antimony; Titanyl Chlorides and Phos. Oxychloride - Ammonia Products |
| C.4 | Antimony Trifluoride |
| C.5 | Antimony Phosphate; Vinyl Chloride resin |
| C.6 | Potassium Dihydroantimoniate |
| C.7 | Copper Antimoniate; Chlorinated Paraffin |
| D. | Titanium compounds |
| D.1 | Titanium Tetrachloride - Antimony Oxide products |
| D.2 | Titanium Chloride Acylate |
| D.3 | Titanium Chlorides |
| D.4 | Titanyl Sulfate |
| D.5 | Titanium and Iron Pyrophosphates for Cellulose Acetate Fibers |

## TABLE OF FIRE RETARDANT CHEMICALS

| | |
|---|---|
| E. | Zinc |
| E.1 | Ammoniacal Zinc; Chlorinated Hydrocarbons |
| F. | Misc. Metal-containing Combinations |
| F.1 | Metal Oxide; Urea; Amine Phosphate Combinations |
| F.2 | Ethylsilicate; Vinyl Copolymers |
| F.3 | Aluminum Sulfate; Lead Acetate; Amine Treatments |
| F.4 | Calcium Alginate |
| F.5 | Alkali Metal Formates |
| F.6 | Organo-Tin Polyesters |
| G. | Amine - Phosphorus Products |
| G.1 | Ammonia; Polyamine Reaction Products |
| G.1.1 | Phosphorus Oxychloride - Ammonia Reaction Products |
| G.1.2 | Phosporus Oxychloride; Ammonia; Ethylenediamine Reaction Products |
| G.1.3 | Phosphorus Pentoxide; Ammonia Products |
| G.1.4 | Phosphoric Acids; Alkylene Polyamine; 2, 3 - Dibromosuccinic Acid Reaction Products |
| G.1.5 | Phosphoric Acid - Amine Condensation Products - |
| G.2 | Aminoplast Phosphates |
| G.2.1 | Phosphoric Acid - Melamine - Dicyandiamide |
| G.2.2 | Dicyandiamide; Formaldehyde Phosphates |
| G.2.3 | Urea; Formaldehyde; Phosphoric Acid; Pyridines |
| G.2.4 | Urea; Pyrophosphoric Acid Products |
| G.2.5 | Urea; Glycerine; Phosphoric Acid Products |
| G.2.6 | Guanylmelamine Pyrophosphate |
| G.2.7 | Methylol Melamine; Aliphatics |
| G.2.8 | Methylol Melamine; Phosphonamides |
| G.3 | Phosphoric Acid, Polyvinylpyridine |

## TABLE OF FIRE RETARDANT CHEMICALS

| | |
|---|---|
| H. | Aziridines APO, APS |
| H.1 | Tris - (1-aziridinyl) Phosphine Sulfide<br>Synonyms: N, N' N" - Triethylene Thiophosphoramide<br>APS |
| H.2 | Tris - (1-aziridinyl) phosphine oxide<br>Synonyms: N, N', N" - Triethylene Phosphoramide<br>APO |
| H.3 | Aziridines with Amines |
| H.4 | Aziridines with Glycols |
| H.5 | APO - Methylol Phosphorus Polymers |
| H.6 | APO - Sulfur-Phosphorus Containing Polymers |
| H.7 | Aziridines with Carboxyalkyl Cellulose |
| H.8 | APO with Anhydrous Ammonia - Phosphorus Pentoxide Reaction Products |
| H.9 | APO with Diammonium Phosphate Solutions |
| H.10 | APO with Sulfamides |
| H.11 | APO; Thiourea |
| H.12 | Phosphine derivatives |
| H.12.1 | Monocarbamol - Substituted Tertiary Phosphines |
| H.12.2 | Methylol Derivatives of Tris (2-Carbamoylethyl) Phosphine |
| H.12.3 | Aziridinyl N-Alky Phosphinic Amides |
| I. | Methylol - Phosphorus Polymers, THPC |
| I.1 | Tetrakis (hydroxymethyl) Phosphonium Chloride |
| I.2 | Tetrakis (Hydroxymethyl) Phosphonium Hydroxide |
| I.3 | THPC with methylol Melamine |
| I.4 | THPC with Urea |
| I.5 | THPC with Ammonia |
| I.6 | THPC with Tris (2-Carbamoylethyl) Amines |
| I.7 | THPC with Tris (Carbamoylethyl) Phosphine and Phosphoroxytriamides |
| I.8 | THPC with Triallyl Phosphate and Phosphonitrilic Chloride |
| I.9 | THPC with Urea and formaldehyde |

## TABLE OF FIRE RETARDANT CHEMICALS

I.10 THPC with Polyvinyl Chloride and Antimony Oxide

I.11 THPC with Polyvinyl Chloride and Chlorinated Paraffin

I.12 THPC with Polyvinyl Chloride, Polysiloxane, and Zirconium Acetate

I.13 THPC with Bromine containing Resins e.g., Polybromo Esters of Phosphonitrilic Halides

I.14 THPC with Melamine and Formaldehyde

I.15 THPC and Diisocyanate Reaction Products

J. Phosphonitrilic Chlorides

J.1 2,3 - Dibromopropyl Esters of Phosphonitrilic Chlorides

J.2 Phosphonitrilic Chlorides and Alkenyl Esters - Polyhalohydrocarbon Adducts

J.3 Phosphonitrilic Chlorides - Hydroxy and Hydrazino Substituted Products

J.4 Phosphonitrilic Chlorides - reaction with Methy Alcohol and Ammonia

J.5 Phenyl Phosphonitrilic Polymers

K. Triallyl Phosphates and Phosphonates

K.1 Triallyl Phosphate - Monomeric

K.2 Brominated Triallyl Phosphates

K.3 Brominated Phosphates

K.4 Haloalkyl Phosphate - Amino Resins

K.5 Triallyl Phosphates - Halogenated Polymers

K.6 Polybromo Phosphate Polymers

K.6.1 Bromallyl Phosphate  
Synonyms: BAP  
Brominated Polymeric allyl Phosphate Ester

K.6.2 Triallyl Phosphate - Polyhalomethane Polymers

K.6.3 Brominated Phosphonate Polymers

K.6.3.1 Tris (2-3 dibromopropyl) phosphate

K.7 Triallyl Phosphates - Nonhalogenated Polymers

## TABLE OF FIRE RETARDANT CHEMICALS

| | |
|---|---|
| K.7.1 | Diallyl Cyanoethane Phosphonate Polymers |
| K.7.2 | Diallyl Carboxymethyl Propanephosphonate Polymers |
| K.8 | Phosphonates and Phosphates |
| K.8.1 | Bis - (2-Bromoethyl) -2-Bromoethane Phosphonate |
| K.8.2 | Bis - (2,3 - Dihalopropyl) Chlorophosphonate |
| K.8.3 | Bis (2-Haloalkyl) Alkenyl Phosphonates |
| K.8.4 | Bis (Bromochloropropyl) Bromo - Chloropropylphosphonate - Cellulose Acetate |
| K.8.5 | Phosphonomethyl Ethers |
| K.8.6 | Diethyl Chlorophosphate Phosphorylation |
| K.8.7 | Phosphorus Esters and Polyesters |
| K.8.8 | Tris (2,2,2 - Tris (Chloromethyl) Ethyl) Phosphate |
| K.8.9 | 2- Phosphotoethyl Ethers |
| K.8.10 | Mesyl -6- Halo - Cellulose Derivatives |
| L. | Silicones |
| L.1 | Aminoplasts Containing Silicon |
| L.2 | Quaternary Ammonium Salt Derivatives of Silicon Compounds |
| L.3 | Polymeric Silicone Resins |
| M. | Isocyanates |
| M.1 | Phosphous, Phosphoryl Triisocyanates |
| M.2 | Polyisocyanates |
| M.3 | Polyvinyl Alcohol |
| M.4 | Diethyl Phosphoric Acid |
| M.5 | Tolylene Diisocyanate Dimer |
| N. | Phosphono Carboxamides<br>Synonym: Phosphonoalkanoic Amides |
| O. | Halocycloalkenyl Acyl Halides |
| P. | Synthetic Polymers |

# TABLE OF FIRE RETARDANT CHEMICALS

| | |
|---|---|
| P.1 | Nylon Flame Retardants |
| P.1.1 | Dimethylol Ethylene Urea - Thiourea |
| P.1.2 | Urea - Thiourea - Formaldehyde Resins |
| P.1.3 | Aminoplast - Melamine - Carbohydrate Formulations |
| P.1.4 | Ammonium Bromide and Aminoplast Resins |
| P.1.5 | Nomex |
| P.2 | Acrylics |
| P.2.1 | Urea - Formaldehyde and Ammonium Bromide Formulations |
| P.2.2 | Phytic Acid - Urea |
| P.2.3 | Hydroxylamine Sulfate and Urea-Formaldehyde, Melamine Resins |
| P.2.4 | Modified Acrylic Fibers |
| P.2.5 | Carbonized Polyacrylonitrile Impregnated Cellulose |
| P.2.6 | Chlorinated Atactic Polypropylene on Non-woven fabrics |
| P.2.7 | Phosphorylated Polyvinyl Alcchol Fibers |
| P.3 | Vinyl Halides |
| P.3.1 | Vinyl Chloride |
| P.3.2 | Vinyl Bromide |
| Q. | High Temperature Aromatic Polymers |
| Q.1 | Nomex |
| Q.2 | Kapton |
| Q.3 | Polybenzimidazole |
| Q.4 | Phenolics |
| Q.4.1 | Novolaks |
| Q.5 | Brominated Bisphenol A |
| Q.6 | Polybrominated Biphenyl |
| Q.7 | Biphenyl ethers |

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